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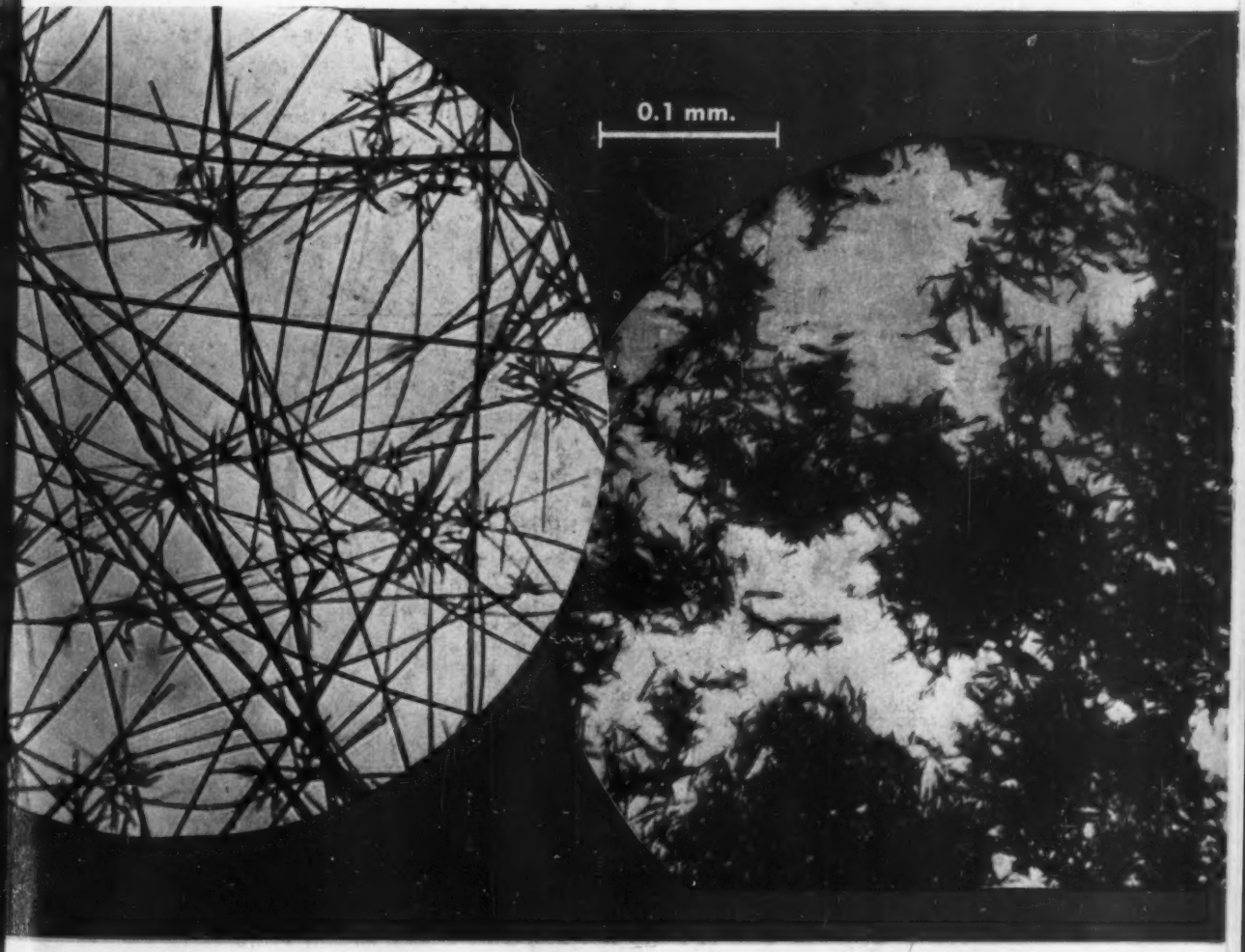

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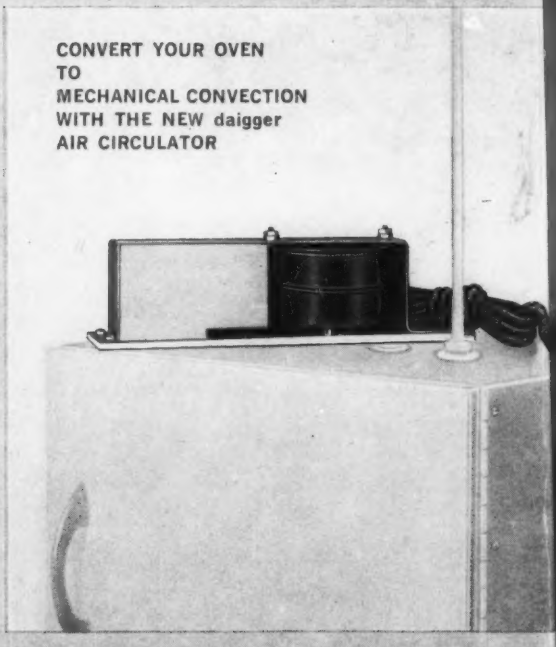

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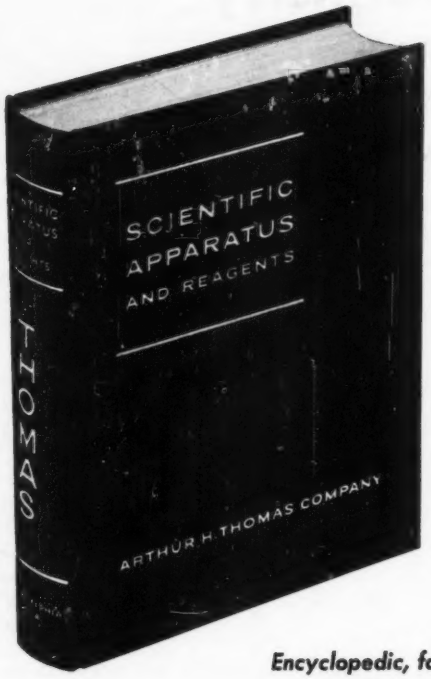

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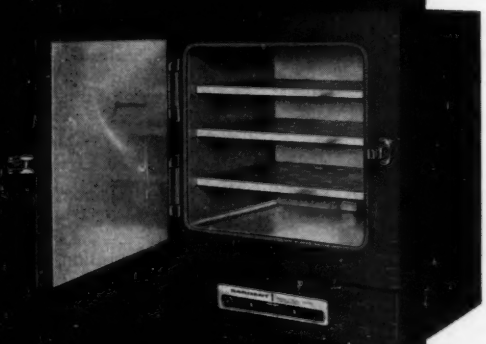

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This series of articles presents a survey of the basic principles, characteristics, and limitations of those instruments which find important applications in chemical work. The emphasis is on commercially available equipment, and approximate prices are quoted to show the order of magnitude of cost of the various types of design and construction.

11. Infrared Spectrometers (Cont'd)

Effect of Design on Performance

Although the double-beam, optical null balance recording spectrometer is at present the most commonly used and widely distributed representative of this category of instrumentation, it does not, and probably never will, completely displace the other types of design. The double beam system is particularly appropriate for rapid-scan, qualitative surveying of spectral characteristics, but there are still many quantitative problems that are best approached through the use of a single-beam instrument. Even within the category of double-beam spectrometers, the optical null balance design is not the only, nor in many applications the best approach to the rapid production of reliable spectra. An alternative design that has many attractive features is the direct ratio recording spectrometer.

The greatest advantage of the double-beam approach in infrared work is dramatically illustrated by the curves reproduced in Figure 14. These show how the single-beam spectra for (*1*) the instrument atmosphere, and (*2*) the same, plus a sample, must be successively determined, lined up, and the spectrum of the sample deduced from these raw data. In the case of the spectra shown in the figure, the time taken to run the curves over the range 2.5 to 16 μ was 50 minutes; the time expended in calculating and plotting the spectrum of the sample by point-by-point division was 4 hours. The double-beam design, by contrast, performs this computation automatically as the spectrum is being scanned, and reads out the desired difference spectrum directly.

However, the convenience of this direct read-out is not obtained without generating many difficult instrumental problems. The essence of the double-beam design resides in the ability of a detector to sense in a sufficiently rapid, sensitive, and reproducible way the difference between the signals in the reference and sample channels. In the optical null balance design, this difference sets in motion a chain of events that attempts to reduce the difference to zero. The accuracy and reproducibility of the spectra read out in this way depend upon the speed and sensitivity of the detector and amplifier, and the freedom from friction, inertia, and distortion of the driving motor and associated mechanisms. The advantages of this optical null principle over other approaches to the implementation of the double-beam design are that since the final state is a balanced one (the difference in the two beams being reduced to a null), the read-out is not sensitive to variations in the characteristics of the light source, detector, and amplifier, and is independent of any non-linearities in these components.

The other approach to the design of a double-beam spectrometer is the direct ratio recording system. Here, no attempt is made to achieve a physical equalization of the two beams; instead, the ratio (or, if desired, the difference) of the intensities is read out after suitable amplification. In this case there are no moving parts, and hence no problems due to wear, vibration, friction, and inertia. Instead, the accuracy and reproducibility of the spectra depend upon the stability and linearity of the electronic circuitry.

Thus, an optical null design places the burden of optimum performance on the optico-mechanical circuit, and relatively simple, inexpensive electronics can be employed. The direct ratio recording design places the burden on the electronics, with consequent simplicity and economy in the optico-mechanical train.

The direct ratio recording design is capable of being applied to very fast recording problems, where the inertia in an optical null system would seriously distort the read-out. Also, the direct ratio scheme permits the signals in the two beams to be amplified independently of each other, and then combined in a variety of ways, giving a greater degree of versatility in data presentation than is available with the optical null technique. On the other hand, the optical null design generally provides better long range stability, and is easier to maintain.

The double-beam, optical null spectrometer is generally best for the routine collection of spectra under standardized conditions, such as in the identification of organic compounds. The double-beam, direct ratio recording spectrometer is often preferred in research applications, or in specialized quantitative determinations, where its speed and/or flexibility are advantageous.

The preceding considerations deal with the relationship between type of design and the accuracy, stability, and reproducibility of the signal read out by the photometer section of the instrument. Equally important in a spectrometer are considerations of the spectral purity of the signal; i.e., dispersion, resolution, spectral slit widths, scattered radiation, etc.

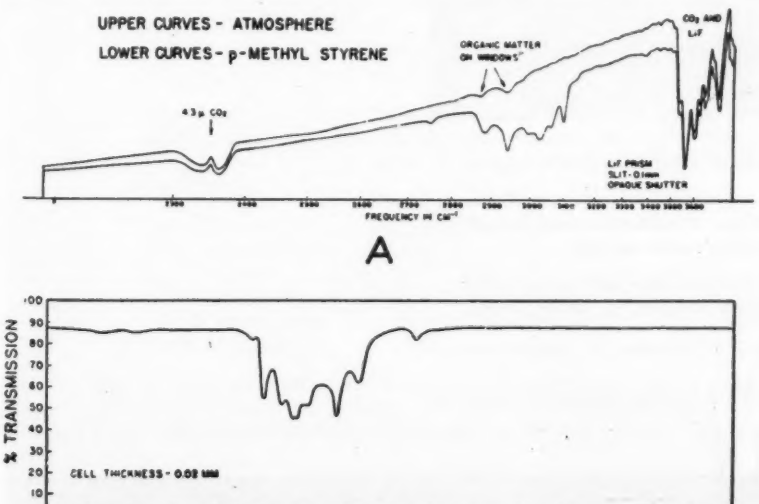

Figure 14. *A.* **Spectra run on a single-beam infrared spectrometer. Upper trace is instrument background; lower trace is background plus a sample of p-methyl styrene.** *B.* **Computed spectrum of the sample, obtained by point-by-point calculation from the two single-beam curves. (From Barnes, *et al.*, *J. Appl. Physics*, 16, 77 (1945).)**

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Band Pass

The *spectral slit width* of a spectrometer is defined as one-half of the total frequency (or wavelength) interval passing out the exit slit. It represents a frequency difference which can exist between two monochromatic bands such that the instrument just fails to resolve them. For the case of a spectrometer employing a Littrow mount and assuming a non-absorbing prism at minimum deviation and perfect optics, the spectral slit width, $\Delta\nu$, is given by:

$$\Delta\nu = \underbrace{\frac{\nu^2(1 - n^2\sin^2\alpha/2)^{1/2}}{4\sin(\alpha/2)\cdot(dn/d\lambda)}\cdot\frac{S_1 + S_2}{f}}_{A} + \underbrace{F(S)\frac{\nu}{2\,b\,(dn/d\lambda)}}_{B}$$

where n is the index of refraction of the prism at frequency ν, α is the prism apex angle, $dn/d\lambda$ is the dispersion of the prism, at frequency ν, S_1 and S_2 are the mechanical slit widths in cm, f is the focal length in cm, b is the effective length of the prism base in cm, and $F(S)$ is a function of the mechanical slit width that is close to 1 under the conditions commonly employed. Term A in this equation corresponds to the spread in frequencies resulting from the finite sizes of the slits and the dispersion of the prism, and increases with increasing slit opening. Term B is constant for a given instrument, and corresponds to the limiting resolving power of the prism, assuming the Rayleigh definition of resolution (i.e., two lines are considered just resolved when the central band of the diffraction pattern of one falls on the first dark band in the diffraction pattern of the second). Figure 15 shows the relative magnitudes of these terms for a typical spectrometer (f = 27 cm) employing a 60° NaCl prism and assuming $S_1 + S_2 = 0.1$ mm.

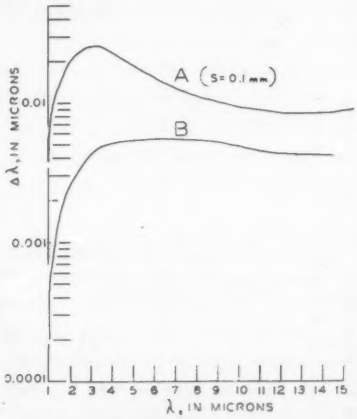

Figure 15. Spectral slit width as a function of wavelength for a spectrometer with a 60° NaCl prism. Curve A shows the contribution to total spectral slit width due to mechanical slit widths of 0.1 mm; curve B shows the contribution due to the limited resolving power of the prism.

The mechanical slit width that must be used at any frequency is determined by

(*Continued on page A8*)

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the energy available from the source, the light-gathering efficiency (speed) of the optical train, the sensitivity of the detector, and the noise level of the detector and associated electronics. In order to operate at a signal-to-noise ratio of 50:1 or greater, it is necessary in infrared spectrometers to employ mechanical slit widths that make term A in the above equation larger than term B. Hence, the spectral slit width, or band pass, in these instruments is said to be *energy-limited*. By contrast, the spectral slit width in visible and ultraviolet spectrometers is generally limited by the inherent resolving power of the prism (term B in the above equation).

An improvement in the purity of the light signal by a reduction in the spectral slit width, but more importantly by the rejection of the scattered radiation that passes through the slit along with the dispersed band, can be accomplished by the use of *double-pass* optics. The principle of this technique is illustrated in Figure 16. Figure 16*a* shows the conventional single-pass Littrow system, with light entering through slit S_1, suffering two dispersions in the prism, and emerging through slit S_2. The light is chopped before entering S_1 and all the radiation emerging through S_2 (including scattered light from dust and surfaces in the monochromator) is sensed by the detector. In Figure 16*b*, the double-pass feature has been added, consisting of a chopper and a right-angle mirror. Unchopped light enters through slit S_1 and is directed into the Littrow-mounted prism. Upon emerging from the prism (after two dispersions), the light is chopped and redirected by the right-angle mirror back to the prism, where it suffers two additional dispersions, and emerges heading for the exit slit S_2. Thus, the light seen through S_2 may contain scattered radiation, but if this was produced before the second pass, it is unchopped, and the ac amplifier will not see it. For a given slit width, the double-pass system gives double the dispersion of the radiant energy, and eliminates much of the scattered radiation from the monochromatized light. The effectiveness of this arrangement in increasing the amount of information that can be read out by the detector is illustrated in Figure 17, which also shows the role of the resolving power of the prism.

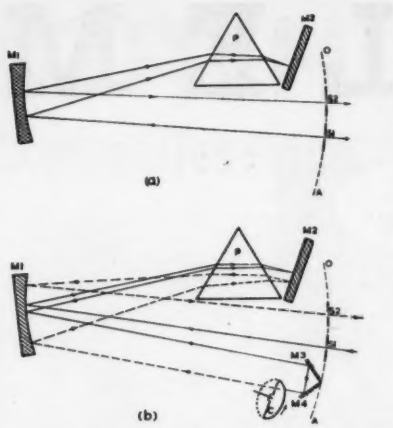

Figure 16. Principle of the double-pass spectrometer design. A. Single-pass arrangement, with chopped light entering slit S_1 and emerging from slit S_2 after undergoing two dispersions in the Littrow-backed prism. B. Double-pass arrangement, with unchopped light entering S_1, being chopped after two dispersions in the prism, and being returned for a second passage through the prism before emerging through S_2.

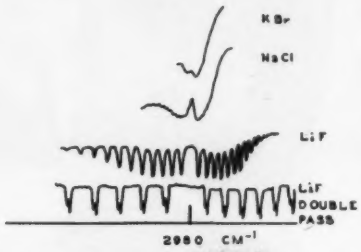

Figure 17. Spectra of the 3.46 micron band of HCl obtained under various conditions of dispersion, illustrating the role of prism material, and of single-pass *versus* double-pass design.

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The most extensive line of commercial spectrometric equipment is manufactured by the Perkin-Elmer Corporation, Norwalk, Connecticut. The models of monochromators and spectrometers currently

(*Continued on page A10*)

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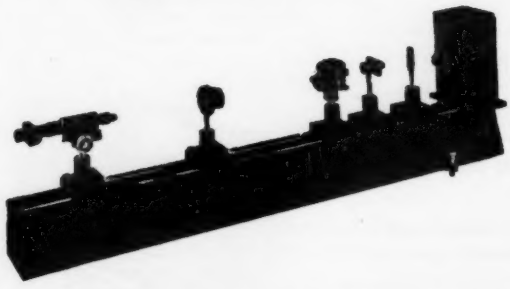

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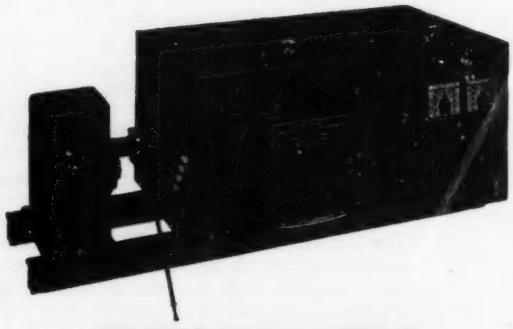

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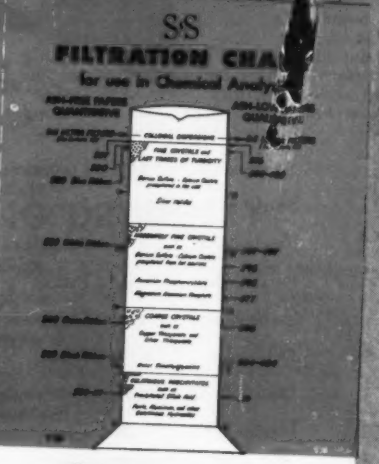

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Ash per circle (in milligrams)	.91	.815	.88	.84	.86	.835	.81

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TABLE
Summary of Perkin-Elmer Infrared Instrumentation

Model	Channels	Passes	Dis-perser	Photom-eter	Price
98 (monochromator)	...	Single	Prism	...	$ 2,350
98G (monochromator)	...	Single	Grating	...	2,175
99 (monochromator)	...	Double	Prism	...	3,150
99G (monochromator)	...	Double	Grating	...	3,075
160 (monochromator foreprism, for use with 98G or 99G monochromators)					2,650
108A (rapid-scan monochromator)		Double	Prism	...	10,000
210 (far IR) (monochromator)		...	Grating	...	7,700
12C	Single-beam	Single	Prism	Direct recording	9,950
12G	Single-beam	Single	Foreprism + grating	Direct recording	11,950
112	Single-beam	Double	Prism	Direct recording	10,550
112G	Single-beam	Double	Foreprism + grating	Direct recording	12,450
112U	Single-beam	Double	Prism	Direct recording	12,800
112UG	Single-beam	Double	Foreprism + grating	Direct recording	17,250
13	Double-beam	Single	Prism	Ratio recording	13,950
13G	Double-beam	Single	Foreprism + grating	Ratio recording	16,200
13U	Double-beam	Single	Prism	Ratio recording	16,950
13UG	Double-beam	Single	Foreprism + grating	Ratio recording	21,500
205 (diffuse reflectance and emissivity attachment for model 13)					13,550
21	Double-beam	Single	Prism	Optical null	10,950
221	Double-beam	Single	Prism	Optical null	14,700
221	Double-beam	Single	Prism + grating	Optical null	15,585
137B NaCl	Double-beam	Single	Prism	Optical null	4,500
137 KBr	Double-beam	Single	Prism	Optical null	4,650
137G	Double-beam	Single	Grating	Optical null	6,300

available from the company are listed in the accompanying Table.

The Model 12C single-beam spectrometer is one of the simplest of the infrared instruments, consisting of a standard Perkin-Elmer source unit, a monochromator, and a photometer. These units are interchangeable with other units and can be attached to other instruments in the Perkin-Elmer line. The optical circuit is shown schematically in Figure 18. Light from a Globar, S_0, is chopped by the rotating shutter, CH, and focussed by front-surface mirror M_2 onto the entrance slit of the monochromator, S_1. The sample compartment, C, is between the source and monochromator units. The light diverging from slit S_1 is rendered parallel by the collimating (paraboloid) mirror M_3, and is sent to the prism, P, with its Littrow mirror, M_4. The light returning from the prism is then focussed by M_3 onto the exit slit, S_2, through which it passes into the photometer section. The focussing (ellipsoidal) mirror, M_7, directs the light onto the thermocouple detector, T.

The construction of the thermocouple is shown in Figure 19. The active metal pair consists of (1) the two pins which are attached to one of the silver leads, and (2) the fine wire which is attached to the other lead. Thermal contact between these active metals is provided by a piece of gold leaf, which is blackened to improve its absorptivity. When radiant energy, J, falls on this leaf, its temperature is raised until a steady state is reached wherein the heat lost from the leaf by radiation and conduction processes just balances the heat input. This temperature rise produces the output voltage, E_0, that is fed to the preamplifier. The thermocouple is contained in a hermet-

(*Continued on page A13*)

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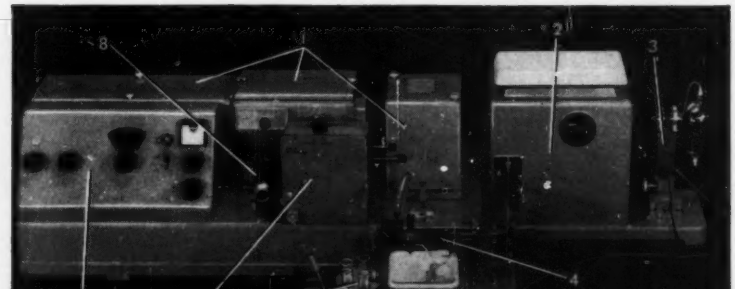

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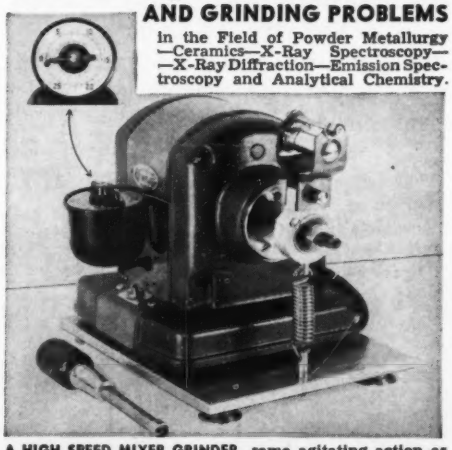

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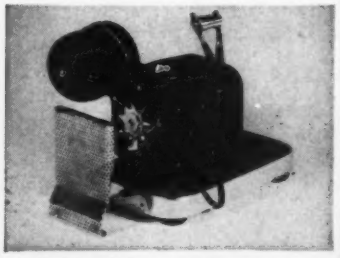
5A—Wonder Electric Mortar—the action is reciprocating in the form of a figure 8 swung through a 6 ½° arc at 3200 RPM, the ball pestle then strikes the end of the vial some 2000 times in ten seconds. Can be run continuously for 5 minutes (and this depends on the load) with a rest period between the 5 minutes to cool the motor completely.



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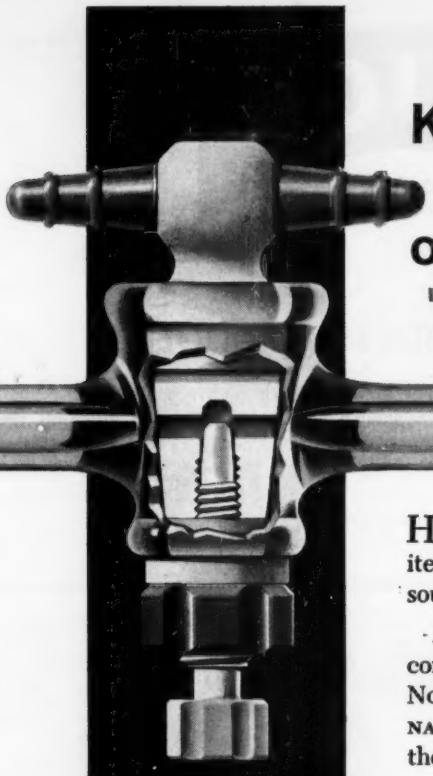

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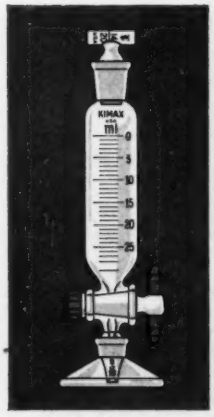

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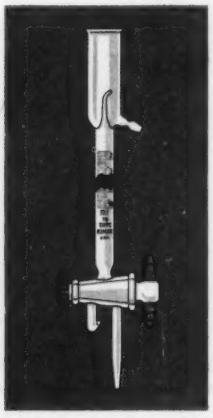

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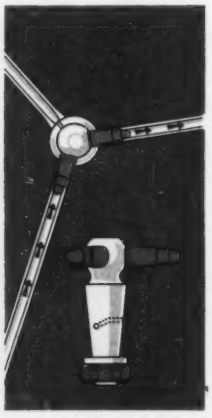

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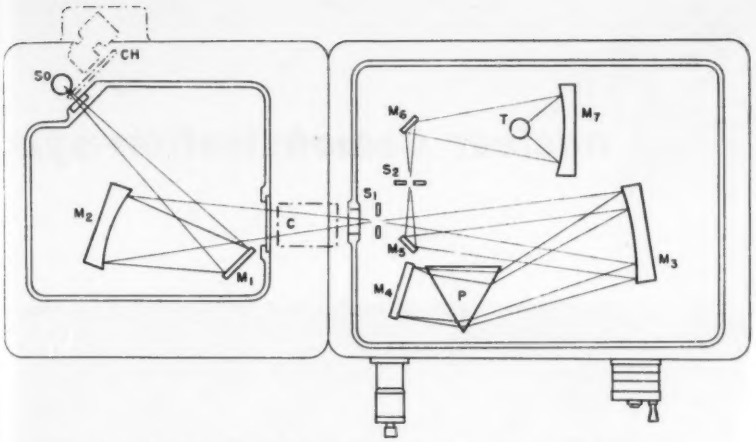


Figure 18. Optical diagram of the Perkin-Elmer single beam Model 12C spectrometer.

ically sealed, evacuated tube provided with a KBr window for entrance of the radiation. The thermocouple enclosure is evacuated to minimize heat losses due to gaseous conduction and convection, which would reduce the sensitivity of the detector. These thermocouples have a thermoelectric power of about 2 microvolts per microwatt. The noise level is of the order of magnitude of 10^{-6}°C, or 10^{-11} watts, or 10^{-9} v, at room temperature.

The detector is a low impedance voltage source, and its output must be fed into a low impedance amplifier. A simplified schematic of the detector and associated electronics is shown in Figure 20. The thermal EMF produced by the thermocouple fluctuates with the frequency (13 cps) of the chopped infrared radiation.

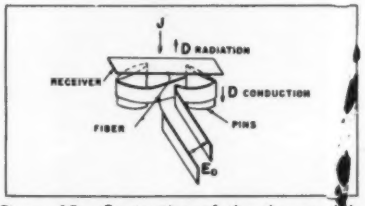


Figure 19. Construction of the thermocouple detector used in the Perkin-Elmer infrared spectrometers. The active metal pair is composed of the fiber and the pins; the receiver is a blackened gold leaf which serves as the thermal and electrical contact between the active metal pair.

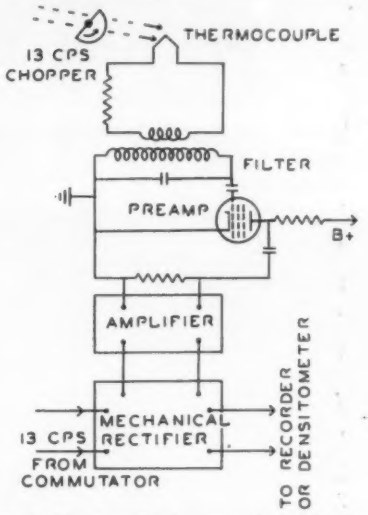
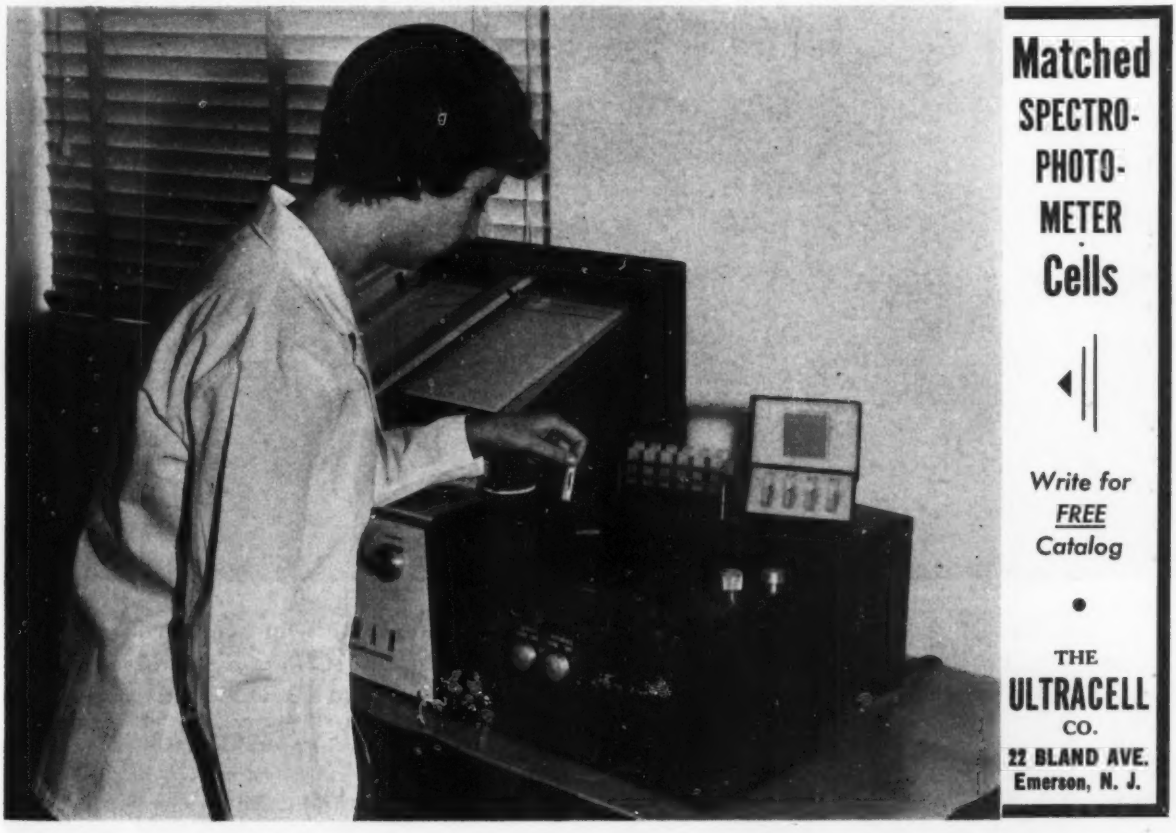


Figure 20. Simplified diagram of the detector-amplifier-read-out circuitry in the Perkin-Elmer Model 12 and 112 spectrometers.

This ac component is passed through the transformer to the grid of the preamplifier. The final amplifier output signal is passed into the mechanical rectifier, where it is demodulated by being mixed with a reference (or "gating") signal of the same

(*Continued on page A16*)



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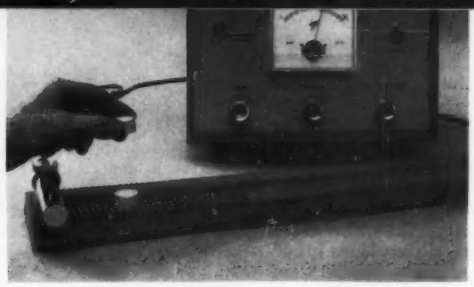
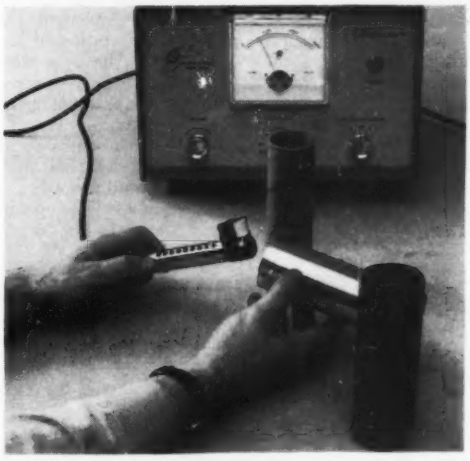
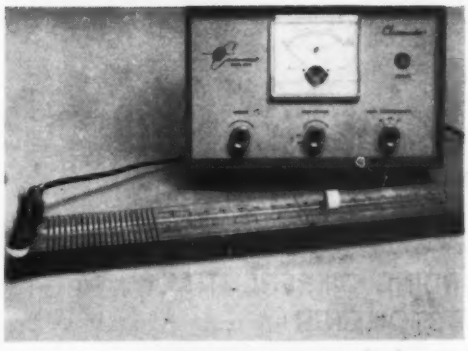


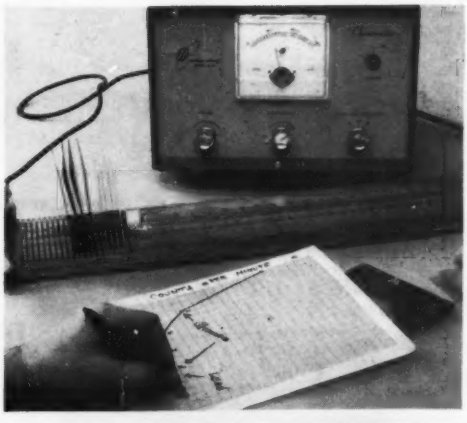
Determining Coincidence Loss



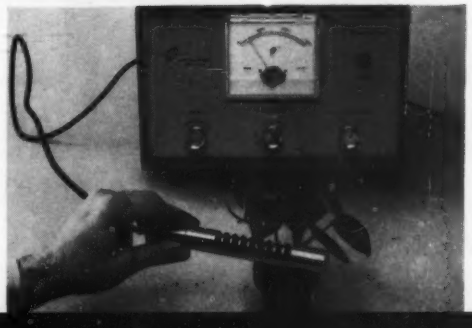
Measuring Radiation Scatter



Counter Plateau and Geometry Effect



Measuring Radiation Absorption



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frequency and phase, derived from commutator contacts on the shaft of the chopper which produced the original ac signal.

The output of the mechanical rectifier may be fed to a potentiometric recorder, or to a densitometer circuit with or without a recorder. When the recorder alone is used, the output signal is balanced against a standard voltage drop on the recorder slidewire, obtained from a reference battery. The densitometer is employed to permit more accurate photometric measurements to be made at a given wavelength. The principle of this device is illustrated in Figure 21. A 13 cps signal is generated by connecting the battery shown to a pair of breaker (commutator) contacts on the chopper shaft. A portion of this ac voltage appears across resistor R_x, and hence opposes the ac voltage generated at the thermocouple, which is in series with R_x. Any difference signal existing is amplified, demodulated, and applied to the null meter, producing a deflection. The sliding contactor on R_1 is then adjusted as necessary to reduce the meter reading to zero, and the position of this balance point is read off in terms of percent transmission on a dial connected to the shaft of R_1. The accuracy attainable is $\pm 0.25\%$ in transmittance.

Wavelength scanning is accomplished by rotation of the Littrow mirror. This may be done manually or by means of a motor-driven mechanism operating at any one of three speeds, or on a 3-speed program.

The entrance and exit slits are ganged together, so that they open and close simultaneously. They may be set at any width opening in the range 0–2000 microns by hand, or may be programmed to maintain a fairly constant bandwidth and I_0 energy level throughout the spectrum. Two programming systems are used: a slit string drive, and a slit servomechanism. In the former, a spiral cut cam is attached to the wavelength drum, and a cylindrical spindle with a helical groove is attached to the slit micrometer shaft. A string is wound on the helical groove of the slit spindle, and its end is attached to the end of the spiral cut cam. As the wavelength drum turns, the string winds up on its cam, and unwinds from the spindle, causing the latter to turn and open the slits. The rate of opening of the slits is programmed by the shape and pitch of the spiral cut cam, increasing as the wavelength increases.

If the slit servomechanism is employed, a servo drive motor is fitted onto the slit micrometer shaft. The degree of rotation of the shaft is caused to increase or decrease as necessary to maintain a constant I_0 level at the recorder.

The resolution of the Model 12C is 1.5 cm^{-1} at 10 μ with an NaCl prism. Wavelength reproducibility is 0.003 μ; transmittance reproducibility is $\pm 0.25\%$.

The Model 112 spectrometer is basically the same instrument described above, but modified to incorporate the double pass principle (see Figure 16). A diagram of the monochromator section of this instrument (also available separately as the Model 99 Monochromator) is given in Figure 22.

Both the single pass and double pass

(*Continued on page A18*)

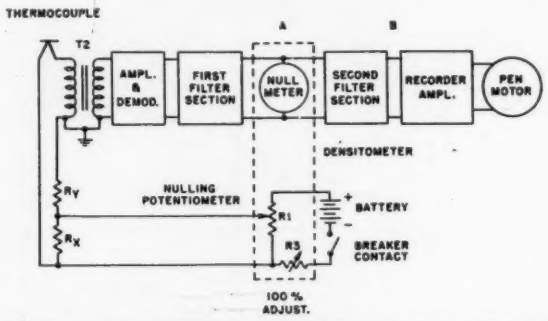

Figure 21. Illustrating the use of the densitometer null-balance read-out applied to the photometer unit of the Perkin-Elmer Model 12 or 112 spectrometers.

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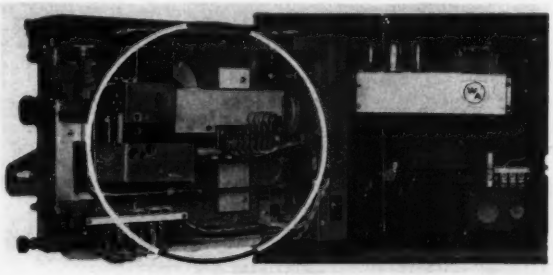

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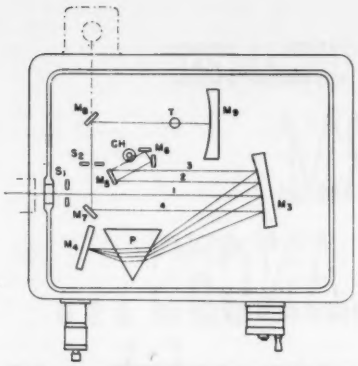


Figure 22. Monochromator unit of the single-beam, double-pass spectrometer.

spectrometers are available with diffraction gratings as the dispersing elements; these instruments are designated Models 12G and 112G, respectively. An optical diagram of the Model 12G is given in Figure 23. Light from the source unit

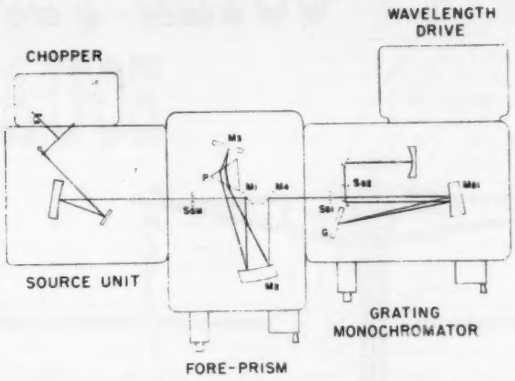
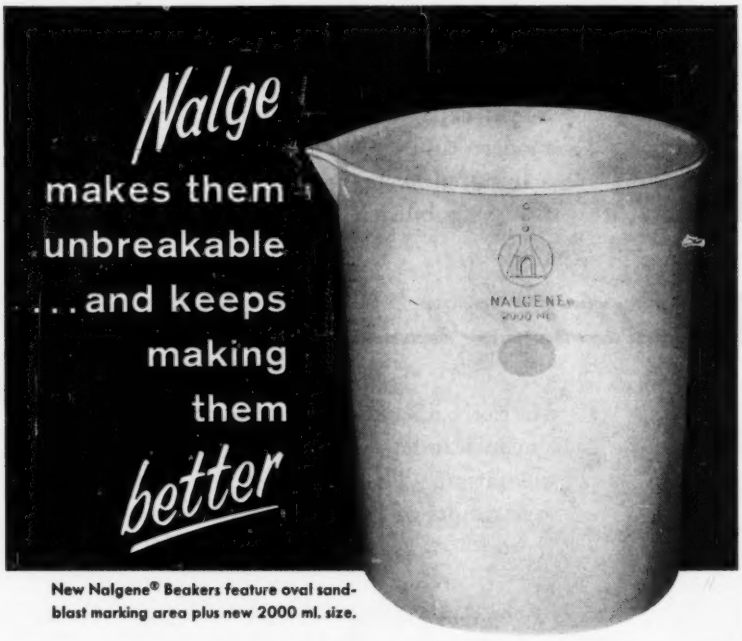


Figure 23. Optical diagram of the Model 12G single-beam foreprism/grating spectrometer.



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enters the fore-prism unit, where it is dispersed so that only a relatively narrow band of wavelengths is allowed to fall on the entrance slit of the grating monochromator unit. The light passing through entrance slit S_{G1} is collimated into a parallel beam by mirror M_{G1}, and directed onto the diffraction grating G. The rays reflected from the grating are focussed by M_{G1} onto the exit slit, S_{G2}.

Figure 24. Design of the echelette diffraction grating used in the Perkin-Elmer Model 12G and 112G spectrometers.

The echelette diffraction grating, illustrated in Figure 24, contains 75 lines/mm and is blazed at 12 microns; i.e., the angle of the grooves is such that the maximum intensity of diffraction in the first order occurs for light of 12 microns wavelength. For a given angle of incidence, and a given angle of reflection, a given diffraction grating will direct onto the exit slit simultaneously a different wavelength of light for each of its orders of diffraction. That is, if the angles are chosen so that light of 12 μ is diffracted in the first order, at the same place there will be found light of 6 μ (2nd order), 4 μ (3rd order), 3 μ (4th order), 2.4 μ (5th order), 2.0 μ (6th order), etc. If a fore-prism is used, so that for example only a band of wavelengths from 2.5 to 3.5 μ is allowed to enter the grating monochromator, then the diffracted light at the exit slit would consist only of the 3 μ of the 4th order of diffraction, and the interference of the other orders will have been eliminated. This is the reason for the requirement of a fore-prism in these instruments.

Since the efficiency of the grating is highest at the blaze angle and falls off rapidly as the angle changes, it is necessary to use five different diffraction orders to cover the 2.2 to 15 micron range. The 5th order spectrum is utilized for wavelengths from 2.2 to 2.6 μ, 4th order for 2.6 to 3.4 μ, 3rd order for 3.4 to 4.8 μ, 2nd order for

(*Continued on page A20*)

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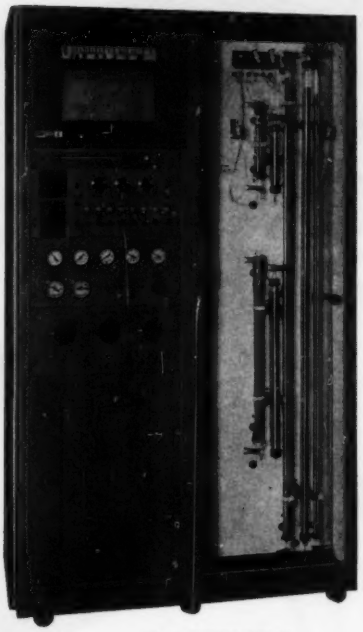

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4.8 to 8.4 μ, and 1st order for 8.4 to 18 μ. These ranges correspond to a total rotation of the grating through 5° in the fifth order; 25° in the first order spectra.

It will be evident from the foregoing that the operation of a fore-prism/grating spectrometer is considerably more complicated than is the case for a simple prism instrument. The advantages of this type of instrument are a great increase in dispersion and resolution throughout the spectral range. Figure 25 shows a portion of the fine structure of the P branch of the 2900 cm^{-1} HCl band obtained with a double pass foreprism grating spectrometer (this spectrum should be compared with those shown in Figure 17).

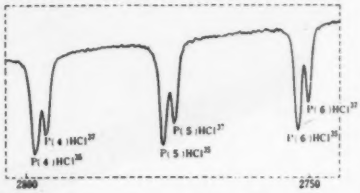

Figure 25. Example of the resolution attainable with a double-pass, foreprism/grating spectrometer. Detail of the 3.46 micron band of HCl.

The Model 112 spectrometer is also available in a Universal form, designated Model 112 U1, which is designed to permit interchange of sources from the Globar to a tungsten filament lamp, to a hydrogen arc. Correspondingly, the NaCl prism can be interchanged with a fused silica prism, and the thermocouple can be interchanged with a lead sulfide (for near infrared) or a photomultiplier detector (for visible and ultraviolet). These facilities make the spectrometer suitable for work in any part of the spectrum from 200 millimicrons to 15 microns.

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MIZUSHIMA, S., *et al.*, "A Report on the Perkin-Elmer Grating Spectrophotometer Model 112-G," published by Perkin-Elmer Corporation, Norwalk, Connecticut, 46 pp., 1959.

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WHITE, J. U. AND LISTON, M. D., "Construction of a Double Beam Recording Infrared Spectrophotometer," *ibid.*, **40**, 29–35 (1950).

Next: Conclusion of the survey of commercial infrared spectrometers.

Kodak reports on:

what Gutenberg might have done with photography . . . new black-and-white film speed numbers . . . an interesting sandwich

Try these paragraphs:

Routine commercial news item: *Kodak Phototypesetting Film* and *Kodak Phototypesetting Paper* are now sold by your* Kodak dealer.

Deeper historical significance: Gutenberg did a fine thing by inventing movable type. The fellows who improved on his idea with hot-lead-casting typesetting machines also did their bit for civilization. Now, however, too many authors want to convey too many complicated thoughts to too many splinter groups of readers. The hot-lead machines are at their best with neat paragraphs of well-carpentered prose. Well-carpentered prose has its place, but for expressing the more severely logical varieties of thought it is limiting, imprecise, unclear, windy, and cumbersome. A more agile symbolism is needed at popular prices. Alert printing houses are trying to provide this symbolism through photographic methods rather than through the brutish hewing of lead. Give them time and encouragement. We have added our little touch of encouragement by having these two paragraphs phototypeset. Whether severely logical or not, they look all right, don't they?

Too conservative

Only conservatives sit on committees that formulate standards for specifying film speeds. They set their lips in thin lines when they overhear enthusiasts trying to top each other with speed numbers. In the '40s they fixed the enthusiasts for fair. They defined the index so as to result in 2½ times the least exposure that even a stern judge would already have to accept as producing negatives of the highest pictorial quality.

They now confess that they leaned over backward too far for minimum grain and maximum sharpness from modern black-and-white films, modern practices, and modern equipment. The following speed numbers are derived from the revised American Standard:

KODAK PANCHROMATIC FILMS	
Sheet Films	**ASA**
Panatomic-X	64
Portrait Panchromatic	125
Super-XX Panchromatic	200
Super Panchro-Press, Type B	250
Tri-X Panchromatic	400
Royal Pan	400
Royal-X Pan	1250
Roll Films	**ASA**
Panatomic-X	40
Verichrome Pan	125
Plus-X Pan Professional	160
Tri-X Pan	400
Royal-X Pan	1250
35mm Films	**ASA**
Panatomic-X	40
Plus-X Pan	160
Plus-X Portrait	160
Tri-X Pan	400

Note that only one figure is given for each film because most meter cells have about the same spectral response as panchromatic film. Two are needed for:

Kodak Blue-Sensitive and Orthochromatic Sheet Films	ASA Daylight	Tungsten
Commercial	50	16
Commercial Ortho	80	25
Super Speed Ortho Portrait	125	64
Royal Ortho	400	250

Aromatic titanium

Eastman 8057
Dicyclopentadienyltitanium Dichloride
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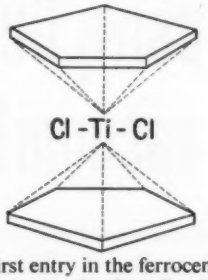
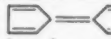


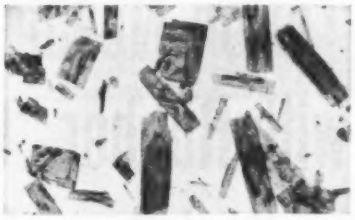
Our first entry in the ferrocene class. That is to say, the first dicyclopentadienyl compound offered as an Eastman Organic Chemical. Have to watch language pretty carefully when mentioning compound reputed to be stereospecific catalyst for polyolefins. Wealth of empires hangs on such things. Nobody make a move, nobody drop or pick up a hint without first consulting his or her patent department.

Academics can afford to be carefreer. Follow knowledge where e'er it leads. Revel in ferrocenes as broadening whole concept of aromaticity in organic chemistry. Benzene, naphthalene, such old-fashioned aromatic nuclei essentially two-dimensional. Here aromaticity enters the third dimension. Whee!!!!

Considerations like zero dipole moment, non-polar nature, single C-H absorption band, x-ray diffraction pattern cinched pentagonal anti-prismatic "sandwich" structure. Real eye-opener. Offspring of casual liaison between two problems: preparation of organo-iron compounds and hunt for route to fulvalene,  .

Soon developed you could have other filling in sandwich besides iron. Funny thing. Our titanium ferrocene has bright, gleaming copper-bronze sheen to it, and original iron ferrocene is also orange-colored. Apparently the color has more to do with the bread than with the filling.

Maybe that's not so funny.



Would have been better to show this in color.

Lot of literature around on ferrocene chemistry. Ran review article on it ourselves in house organ, *Organic Chemical Bulletin, 30,* No. 3, 1958. (Are ferrocenes truly organic? Is it wise to ask?) Didn't even have any ferrocene compounds to sell then. Published it merely because we had ferrocene expert on payroll and wanted to show him off. Still have few leftover copies of that issue. Free while they last.

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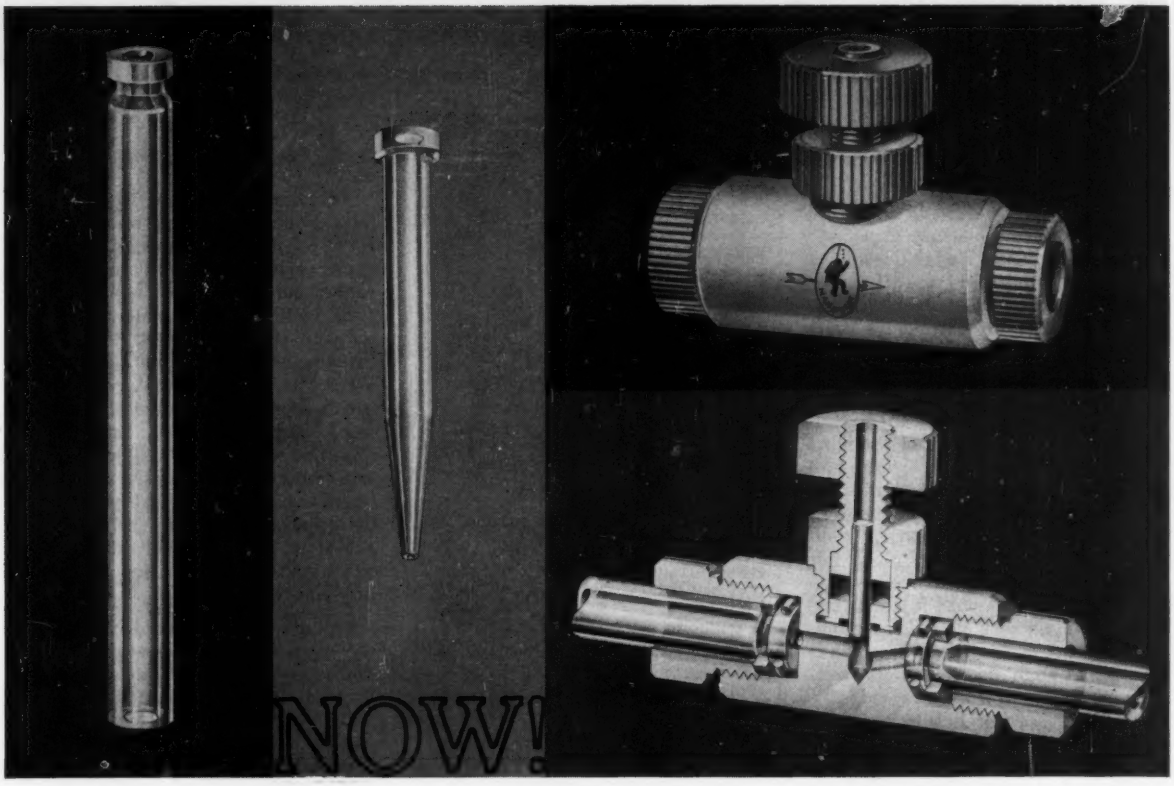
This is another advertisement where Eastman Kodak Company probes at random for mutual interests and occasionally a little revenue from those whose work has something to do with science



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*Trade name for DuPont polytetrafluorethylene
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GRAHAM'S LAW OF DIFFUSION USING OVERHEAD PROJECTOR

A Chem Ed TESTED DEMONSTRATION

Submitted by: Paul Reber, John Adams High School, South Bend, Indiana
Checked by: Julian R. Brandou, Michigan State University, East Lansing

PREPARATION

Provide a glass tube, 10 mm i.d., 25 cm long, and open at both ends; two cotton swabs about 2 cm long and of a diameter to fit inside the tube; two corks to fit the tube; a clear vinyl plastic rule 25 cm long; and aqueous solutions (concentrated) of NH_3 and HCl.

DEMONSTRATION

Place the 25-cm rule on the platform of the overhead projector, adjacent and parallel to the tube. Dip one swab into the HCl solution and the other swab in the NH_3 solution. Immediately place the swabs of cotton in opposite ends of the tube and insert the corks.

REMARKS

Observe the ring of NH_4Cl formed in approximately 60 seconds. Note the position of the ring in relation to the markings on the 25-cm scale and compare data obtained with that predicted by Graham's Law.

DEMONSTRATION NOTES

A Chem Ed TESTED DEMONSTRATION

From time to time items such as the following, which do not require a full half-page, will be listed together. Some of them will be modifications of previously published demonstrations, in which case it is suggested that they be clipped and attached to the pertinent experiment.

COLOR CHANGE WITH TEMPERATURE

Roger Wheaton, demonstration-lecture assistant at Michigan State University, observed that the residue remaining in the Soxhlet extraction apparatus after the completion of the chemical equilibrium experiment described by S. B. Butler ("Tested Demonstration," this Journal, **37**, November 1960) was quite temperature sensitive. A similar solution can be prepared directly by mixing 20 ml of 0.5 *M* $CoCl_2$ solution with 16 ml of saturated NaCl solution. When this mixture is chilled in cold water it turns pink and when heated for a brief time in the Bunsen burner flame will turn blue. The process may be repeated at will.

SUBLIMATION

Dale E. Rose, of Hampton High School, Virginia, suggests plunging a hot copper wire (fastened on the end of a wooden splint) into metaldehyde. The material sublimes readily and re-crystallizes in the air forming beautiful snow-like crystals. The metaldehyde may be synthesized by cooling a mixture of acetaldehyde and a drop of sulfuric acid in an ice salt bath.

BURNING PHOSPHORUS IN AIR

Dr. H. N. Alyea, of Princeton University, suggests the use of a $^3/_8$-in. flat head machine bolt which has a small recess drilled in the end. This recess when filled with red phosphorus makes a free standing support for the phosphorus when demonstrating the removal of oxygen from the air. The bolt may be placed head down in a shallow pan of water and a bottle may be lowered over the phosphorus once it is ignited.

CATALYTIC OXIDATION OF AMMONIA

Clayton Berling of Oakland City College, California, points out that copper wire gauze is a very effective catalyst for the oxidation of NH_3. The use of copper wire gauze in place of platinum or copper wire makes a more spectacular demonstration, especially effective if the room can be darkened slightly.

See: (References are to the 1960 Reprint Edition of "Tested Demonstrations") Alyea, H. N., page 38, 135; State, H. M., page 61; Nechamkin, H., and McClarnon J. J., page 81.

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New Apparatus & Equipment

▶ A Radioactive Decay Rate Slide Rule 5.5 inches in diameter constructed of vinylite plastic that sells for $3 can be purchased from the Dyna-Slide Co., 600 S. Michigan Ave., Chicago 5, Illinois.

▶ Bausch & Lomb, Rochester 2, New York, has introduced the Balomatic 655, a completely new, fully automatic, 2 × 2 slide projector. The 1961 model combines, in one compact design, all of the features most desired in today's market, including: high fidelity picture quality, single slide editing, remote forward/-reverse operation, completely automatic time cycling, and simplified operation.

▶ Will Corporation, Box 1050, Rochester 3, New York, announces a new breakthrough in the application of Ultrasonics to the general laboratory. Available for immediate delivery is a budget-priced, single unit Ultrasonic cleaner, SG-2, designed especially for the hundreds of routine cleaning chores encountered daily in most laboratories.

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▶ Applied Science Laboratories, Inc., 140 N. Barnard St., State College, Pennsylvania, offers SE-30, a coated Gas-Chrom, chromatograph column packing, for complete separation of a cholestane, cholesterol, α-sitosterol, stigmasterol, and a β-sitosterol mixture has been obtained with virtually no tailing.

▶ Spinballs, the latest in stirring apparatus . . . a DuPont Teflon magnetic stirring ball for use in agitating liquids in round bottomed containers are available in 3 sizes; $^1/_2$ in., $^5/_8$ in., and $^3/_4$ in., in diameter from Laboratory Plasticware Fabricators, 714 Baltimore, Kansas City 5, Missouri.

▶ Release of the portable, wide span, multi-range, transistorized, YSI Model 42 Tele-Thermometer −40°C to 150°C and −40°F to 300°F is announced by Yellow Springs Instrument Co., Yellow Spring, Ohio.

▶ Portability, economy of space, and solvent resistance are characteristics of the "Chromatobox," a new chromatography developing chamber for which Research Specialties Co., 200 S. Garrand Blvd., Richmond, California, is the distributor.

The Chromatobox is recommended for laboratories having a small volume of chromatographic work, for individual student instruction, for easy portability to lectures and demonstrations, and as auxiliary equipment for test strips in laboratories having larger chromatography equipment.

▶ The Princeton Division of Curtiss-Wright Corp., Princeton, New Jersey, offers "Thermochrom" crayons and "Dectotemp" paints for measuring surface temperatures.

▶ A stopcock lock without springs or clamps, which provides positive locking action yet permits freedom of rotation, has been introduced by the Glass Products Division, Fischer & Porter Co., 702 Jacksonville Rd., Warminster, Pa.

▶ A newly introduced automatic recording thermobalance performs thermogravimetric studies in vacuum or controlled atmospheres at temperatures to 1000°C.

(*Continued on page A27*)

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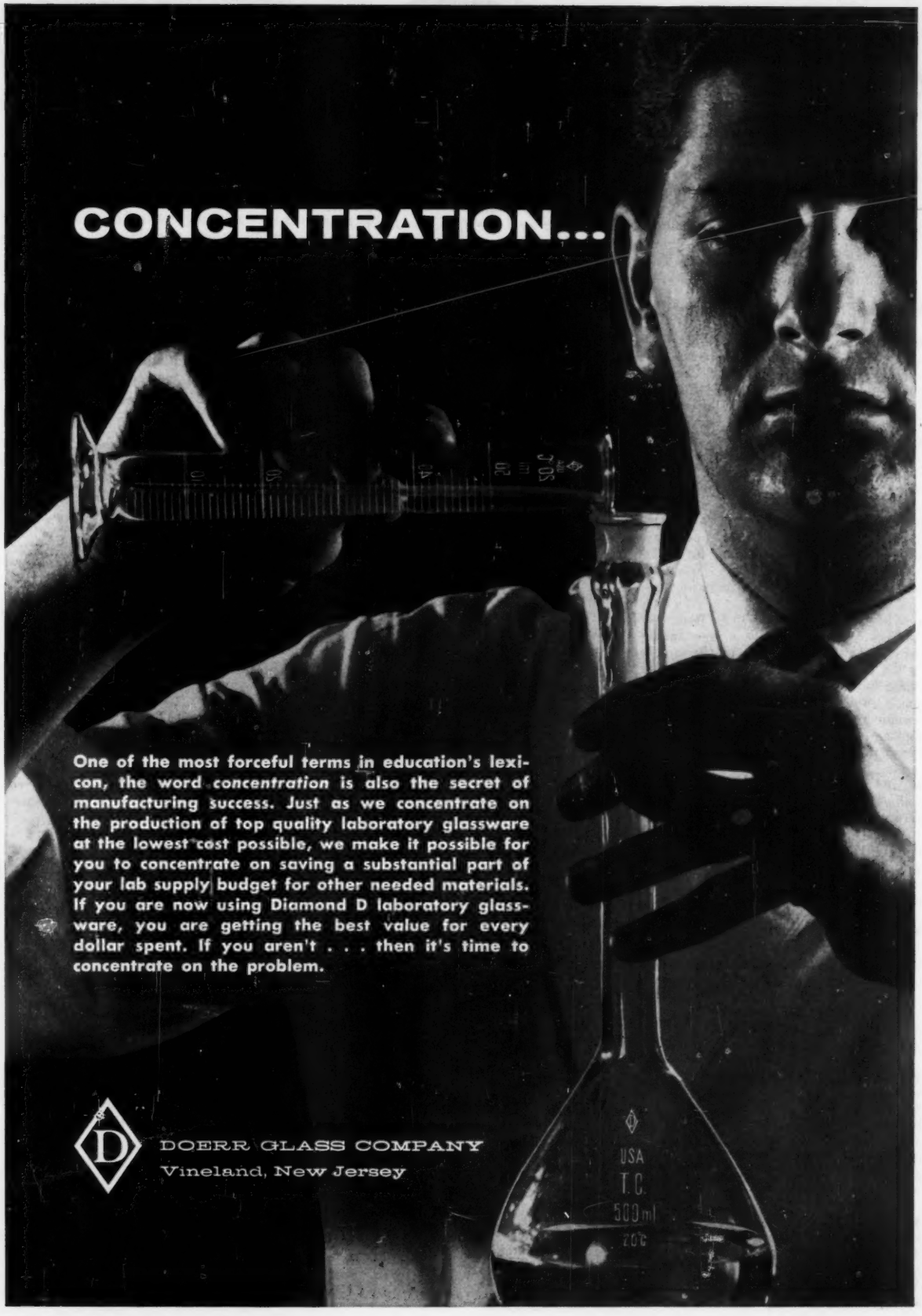
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New Literature

● *Correction:* The *Manual of Simplified Glass Blowing,* mentioned in this column in our September, 1960 issue, may be purchased for $2.00 from Bethlehem Apparatus Co., Inc., Hellertown, Pennsylvania. We were erroneously under the impression that no charge was being made for this publication, and regret any inconvenience caused our readers.

● Copies of Hamilton's *Complete Control Cabinet Catalogue* describing the handling of hazardous materials and maintaining purity are available on request from Dept. 350, Hamilton Manufacturing Co., Two Rivers, Wisconsin.

● A new 16-page stopwatch selection guide describing a complete line of precision timing instruments for all segments of industry, including production analysts, engineers and others in design, testing and control has been announced by Heuer Timer Corp., 441 Lexington Ave., New York 17, N. Y.

● A new, 16-page bibliography of phosphorescent compounds listing over two hundred compounds is now available as a guide to identifying solutions through their phosphorescent properties. The compounds list and *Bulletin 2334,* which describes the Aminco-Keirs Spectrophosphorimeter in detail, are available from the American Instrument Co., Inc., 8030 Georgia Ave., Silver Spring, Maryland.

● The M.C.A. has an excellent new booklet, *Guide to Educational Aids Available From The Chemical Industry,* that should be in every chemistry teacher's file. It lists pamphlets, booklets, books, charts, experiments, and brochures that have been developed by the industry; some are free, others require a small charge. Write to the Manufacturing Chemists Association, Inc., 1825 Connecticut Ave., N. W., Washington 9, D. C., for a copy.

● Production and release of a new Kimax glass pipe catalogue has just been announced by the Fischer & Porter Co., Warminster, Pa.

● For your copy of *Lablog 3-60,* write today to: Will-Lablog, Box 1050, Rochester 3, New York, or contact the nearest Will Center.

● New 16-page *Supplement 2* to LaPine catalogue "Science Equipment for Schools" lists many new items of science apparatus. Request a copy from Arthur S. LaPine and Co., 6001 S. Knox Ave., Chicago 29, Illinois.

● A new 36-page catalogue, describing a

(*Continued on page A30*)

The Improved Welch
CATHETOMETER
For Precise Measurements

Rapid Leveling— Fine Elevation Adjustment
Graduations Engine Divided for Uniformity and Accuracy

Vertical Range	100 cm
Smallest Reading by Vernier	0.05 mm
Telescope	
Working Distance	45 cm to Infinity
Angular Magnification	12X at 45 cm 8X at Infinity
Reticle	90-degree crosshairs
Level Sensitivity	50 Seconds

The latest improved design of the Welch cathetometer possesses a combination of features not hitherto available in an inexpensive instrument. It can be leveled and placed in proper adjustment easily and rapidly, yet all adjustments have sufficient sensitivity and delicacy of control to please the most meticulous user. It is intended for measurements and observations in both industrial and educational laboratories wherever an inexpensive instrument of good precision is needed. It is rigidly constructed and every essential adjustment can be made simply and positively.

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Since 1946 Tracerlab has pioneered in the use of radioisotopes. Tracerlab scientists actually developed many of the techniques basic to this modern analytical method. Tracerlab engineers designed many units that have set performance standards in both education and research. Therefore, if experience and accomplishment are your criteria:

Talk to Tracerlab! You'll soon discover they have available a wide range of instruments and accessories for nuclear education — more than enough to establish well-rounded courses in nuclear techniques. Tracerlab offers scalers, ratemeters, laboratory monitors, detectors, sample changers, survey meters, radiochemicals, reference sources, personnel protection equipment, and numerous other accessories.

If you are not in a position to completely equip your laboratory now, remember that Tracerlab instruments are extremely versatile, making possible a wide variety of classroom demonstrations and laboratory experiments with only a few basic instruments. But most important, Tracerlab equipment is designed and built for constant use in research laboratories and has a ruggedness and quality far greater than that usually offered for educational purposes. (In fact, where research funds are limited, the same Tracerlab instruments can do double duty in education and in research.)

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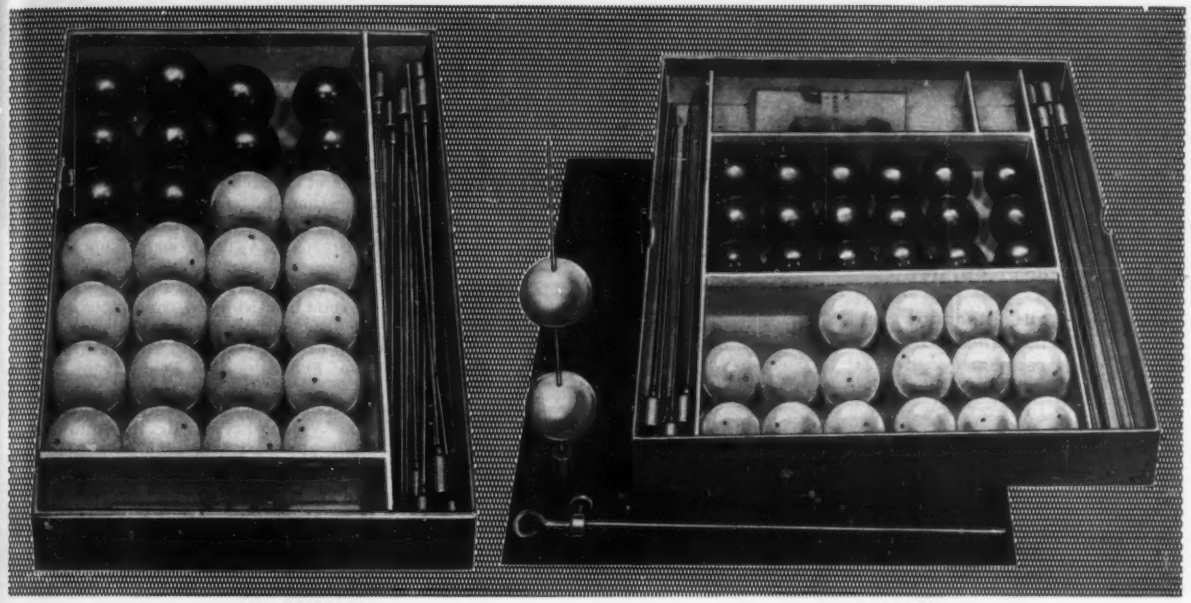
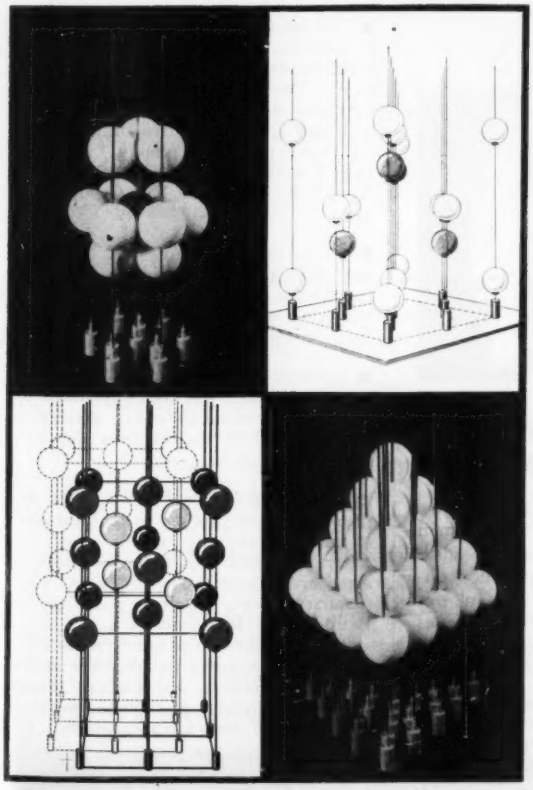


No. CE355-11
Supplementary Lattice Model Construction Kit

No. CE355-10
Lattice Model Construction Kit

Now better learning is possible through LaPINE-Leybold do-it-yourself crystal lattice construction kits.



● These three dimensional models make it possible for students to see and "feel" the spatial characteristics of the important types of lattices.

● When you demonstrate with these kits, and allow actual do-it-yourself assembly by students, they quickly grasp the knowledge presented and display the understanding that is one of the true marks of learning.

● The LaPine lattice model kits provide excellent three dimensional visual demonstration of the crystal structure of matter for mineralogy, solid state chemistry, and physics. Different structure models can be built to show the systematic arrangement of crystals and crystallographic properties, such as periodicity, symmetry, etc. In addition, a small model can be enlarged periodically in the direction of the three coordinates to show origin and growth of crystals. Spheres can be closely packed to demonstrate how space is filled up and the size of holes.

The complete kit contains red and white spheres the size of table tennis balls with two diametrically opposed holes drilled in them, steel needles with magnetic bases, rubber washers to position the balls on the needles, and a steel base plate. The plate can be inclined to show oblique lattice planes from every side.

No. CE355-10 Lattice Model Construction Kit according to Dr. Peter, for building crystal lattice models, consisting of a base plate 30 x 30 cm, an adjusting rod, 18 white and 18 red spheres, 18 steel needles, and 50 rubber washers. **Per Set.....$53.40**

No. CE355-11 Supplementary Lattice Model Construction Kit consisting of 18 white and 10 green spheres, 14 steel needles, and 50 rubber washers. **Per Set.....$34.00**

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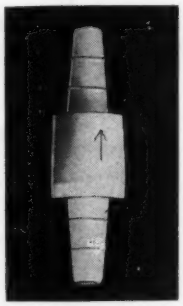

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broad range of nuclear accessories and related instrumentation for radioisotope users in research, industry, medicine, and education, is now available on request from Atomic Accessories, Inc., 811 W. Merrick Rd., Valley Stream, New York.

● A 4-page *Data Sheet E-95(3)* describing two new transistorized, continuous indicating conductivity monitors is available from Leeds & Northrup Co., 4934 Stenton Ave., Philadelphia 44, Pennsylvania.

● Ohio Chemical & Surgical Equipment Co. (A Division of Air Reduction Co., Inc.), 1400 E. Washington Ave., Madison 10, Wisconsin, has announced the availability of their new *Laboratory Gas Mixtures Catalogue.*

● *Bulletin HS,* illustrating scientific equipment designed especially for use in the high school laboratory, has just been released by E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois.

● A 16-page new product supplement which completely up-dates the firms 112-page catalogue has been issued by the Ealing Corp., 40 University Rd., Cambridge, Massachusetts.

● The second issue of F & M's quarterly publication, *Facts & Methods,* features an exclusive article by Dr. Wolfgang Schöniger. Dr. Schöniger writes of the history and development of the technique and uses both illustrative drawings and an extensive bibliography. Available from F & M Scientific Corp., 1202 Arnold Ave., N.C.C. Air Base, New Castle, Delaware.

● Schaar and Company, 7300 W. Montrose Ave., Chicago 34, Illinois announces the release of a new 16 page *Laboratory,* with over 40 timely analytical laboratory items for the chemist.

● A new 22-page catalogue, *Nuclear Products for Industry,* has been announced by Isotopes Specialties Company, division of Nuclear Corp. of America, Box 688, Burbank, California.

● *The Educator . . . and the Atom,* a 46-page booklet reviewing current progress in nuclear training as discussed by government and educational leaders at a symposium held in New York City (January, 1960), has been published by Baird-Atomic, Inc., sponsors.

The booklet contains practical, detailed reports on the use of radioisotopes at the high school, college, and graduate levels; on federal programs of financial assistance to either the institution or student for nuclear training; and on experiments and laboratory techniques with radioisotopes.

Available from Baird-Atomic, Inc., 33 University Rd., Cambridge 38, Massachusetts.

● A handy new 19-page publication

(*Continued on page A32*)

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Laboratory DRYING OVENS

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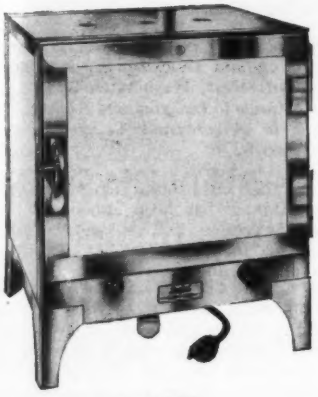

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- 3/8" thick Marinite for temperatures up to 200°C.
- New bimetallic thermostat mounted in heating area for better sensitivity and easy adjustment. Temperature control ±1°C.
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- 660W heating units located in bottom, readily accessible for replacement or changing from 115 V. to 230 V. use.
- Supplied with a three-wire cord and plug.
- AC only—specify 115 volt or 230 volt.

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No. 1078G DRYING OVEN—*same, but with Heat Resisting Glass door.*

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- Polished stainless top and control panel.
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- Strong spotwelded frame.
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- Adjustable bottom ventilators.
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- Working chamber inside 18 1/4" high x 17" wide x 14 1/4" deep.
- Explosion proof door catch with streamlined chrome handle.
- Galvanized expanded metal shelves, bound with stainless steel.
- Overall outside dimensions 25 5/8" x 18 1/4" x 17 1/2" deep.
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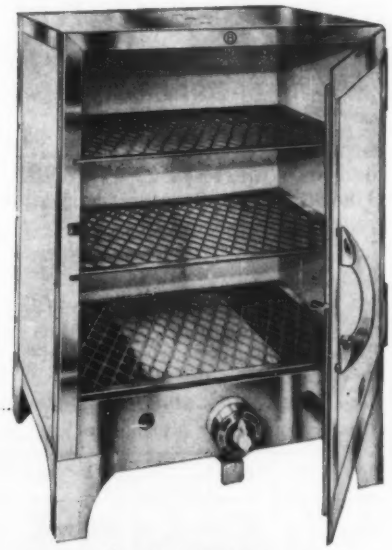

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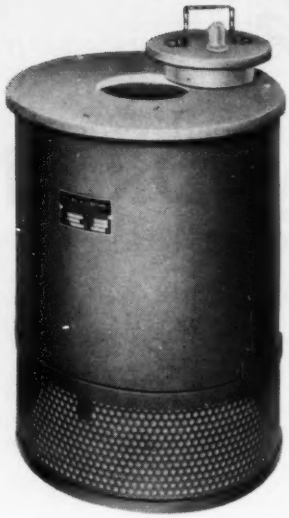
Laboratory technicians using Hevi-Duty Crucible Furnaces find they give the dependable service demanded by exacting research. Improved insulation and sturdy, long-life heating element construction are a few of the advantageous features.

Write for Bulletin 1246.



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Accurate Temperature Control by sensitive bulb-type thermostat permits little lag or overshoot.

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HK	$169.	15	13	600	115/230	20	18	23	80
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listing several hundred compounds exhibiting fluorescent characteristics is now available as a guide to identifying solutions through their fluorescent properties. The compounds list and *Bulletin 2336*, describing the Aminco-Bowman Spectrophotofluorometer in detail, are available from the American Instrument Co., Inc., 8030 Georgia Ave., Silver Spring, Maryland.

● The National Federation of Science, Abstracting and Indexing Services, 301 E. Capitol Street, Washington 3, D. C., offers *A Guide to Indexing and Abstracting Services in Science and Technology*, 79 pages, 1960, $2.

● Publication of the *Duolite Ion-Exchange Manual* has been announced by Chemical Process Co., Redwood City, California, manufacturer of industrial resins, plastics, and adhesives.

Commencing with a section of the general properties and behavior of various types of ion-exchange resins, the manual continues with detailed descriptions of laboratory procedures—including methods for setting up columns, for treating resins prior to use, for determining capacities and for carrying out various physical and chemical tests.

An invocation to usual treatments of the subject is introduced with a section devoted to applications of ion-exchange, arranged according to industry, based on issued patents. Requests for individual copies are being received by Dr. Irving M. Abrams, Chemical Process Co., 1901 Spring St., Redwood City, Calif.

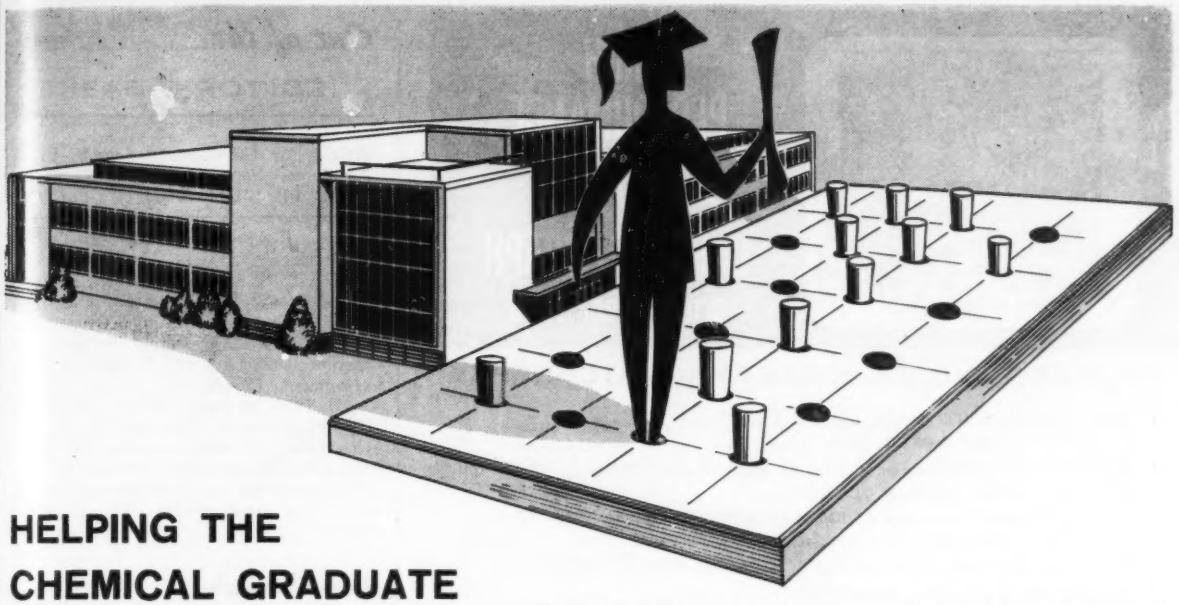
● The Isotope Department of the Weizmann Institute of Science, Rehovoth, Israel, announces availability of a leaflet, *The Stable Isotopes of Oxygen*.

● Diisocyanates—their history, chemistry, and uses in modern-day products—are described in an 8-page booklet published by Allied Chemical's National Aniline Division, 40 Rector St., New York 6, N. Y.

● The following may be ordered from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. *Alphabetical Index to Tables of Chemical Kinetics, Homogeneous Reactions*, National Bureau of Standards Circular 510, Supplement 2, issued August 5, 1960, 37 pages, 35 cents. *Stabilization of Free Radicals at Low Temperatures—Summary of the NBS Program*, edited by A. M. Bass and H. P. Broida, National Bureau of Standards Monograph 12, issued August 1, 1960, 110 pages, $1.50.

● The following may be obtained from O.T.S., U. S. Dept. of Commerce, Washington 25, D. C. PB 161508 *Preparation and Properties of some Polyphenyls.* G. F. Woods, University of Maryland for

(*Continued on page A34*)



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Atlas Powder Company, Wilmington, Delaware, founded January 1, 1913, now maintains 8 plants, 4 research laboratories and 38 sales offices throughout the United States. Atlas is an acknowledged leader in the field of industrial chemicals and explosives. Product lines include commercial explosives, polymers, specialty chemicals, emulsifiers, activated carbons.

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REAGENTS AND CHEMICALS

Out of the EDITOR'S BASKET

Wright Air Development Center, U. S. Air Force. September, 1959, 178 pages, $3.00. PB 161460 *Study of Ultra High Temperatures.* A. V. Grosse and C. S. Stokes, Research Institute of Temple University for Wright Air Development Center, U. S. Air Force. April, 1959, 26 pages, $1.00. PB 161460 *Study of Ultra High Temperatures.* A. V. Grosse and C. S. Stokes, Research Institute of Temple University for Wright Air Development Center, U. S. Air Force. April, 1959, 26 pages, $1.00. PB 161479 *An Experimental Investigation on the Chemistry and Interconversion of Boron Hydrides.* R. Schaeffer, Indiana University, for Wright Air Development Center, U. S. Air Force. July, 1959, 51 pages, $1.50.

New Chemicals

◇ In this day of lease/purchase plans for commercial and industrial equipment, Bio-Rad Laboratories, 32nd Griffin Ave., Richmond, California, has added an exotic item to industry's list—heavy water or deuterium oxide, D_2O. This substance, a component of nuclear reactors and a key material in basic studies involving biological systems and moderation of nuclear-particle paths can be leased for periods ranging from three months to two years at a fraction of the cost of purchasing or producing the material.

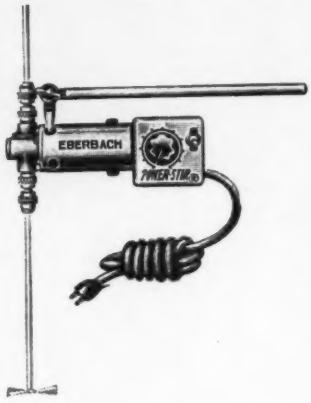
◇ An important new "tracer" compound is now available to biological research workers from New England Nuclear Corp., 575 Albany St., Boston 18, Massachusetts. The compound, thymidine-methyl-H^3, is a precursor of both RNA and DNA and can be employed for investigations of cell growth, genetic patterns, turnover, and etc.

Miscellany

★ The National Institute of Health has placed a grant for the training of students in medicinal chemistry with the Medical College of Virginia. Any student with a bachelor's degree in science may apply; awards will be made on ability and competence. Contact The Dean, School of Graduate Studies, Medical College of Virginia, Richmond 19, Virginia, for further information.

★ "Our Universities: Unguided Missiles" is the title of an interesting article by Jacques Barzun in *Think* for November, 1960. He says, "Next to hospitals, American colleges and universities are the worst administered private establishments in the land. Some faculty members might dispute this ranking and argue that academia deserves first place." He suggests 10 pertinent, concrete suggestions that should be on the desk of all administrators.

(*Continued on page A36*)



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- 3-Wire Cord is Standard

For intermittent heavy duty, the Power-Stir has speeds from 100 to 1000 r.p.m. The 1/10 h.p. motor develops 16 inch-pounds torque thru quiet 20–1 worm gear drive. Power-Stir is hinged on a 1/2″ × 11″ nickel-plated rod and positioned by a large wing nut. Running current, full load is 8 ampere, 115 volt, AC.

No. 7085 Power-Stir	**$32.50**
No. 7400 1/2″ rod with 2″ dia. blade 18″ length	**$ 2.50**

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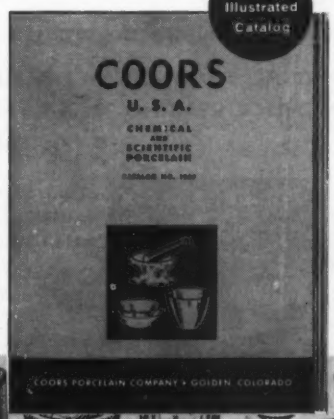

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TRANSPORTATION protects safety, determines need for overhaul by spectro-analysis of diesel oil. Cuts the maintenance and oil bills.
AGRICULTURE tests plant tissues to determine efficiency of fertilizers and pesticides.
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Out of the EDITOR'S BASKET

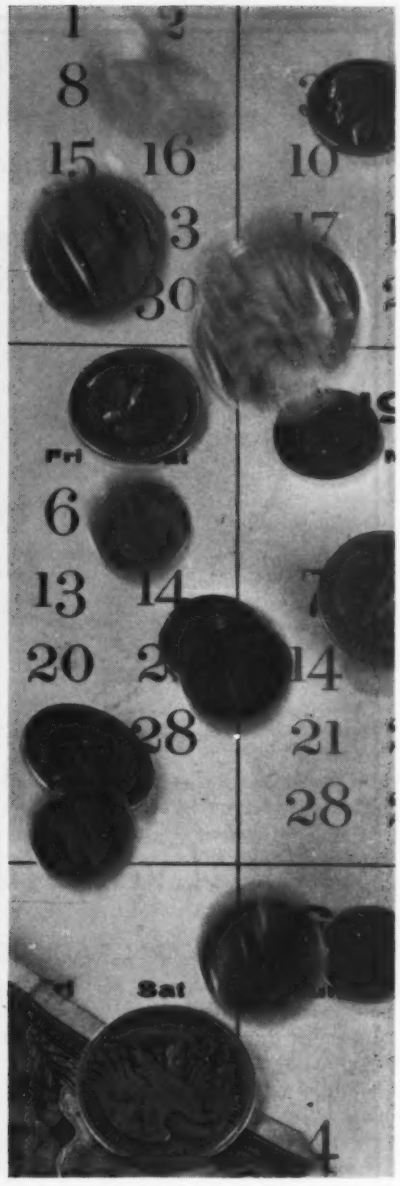
★ Two new Technical Advisory Committees have been established by the National Bureau of Standards, U. S. Department of Commerce, one on Calibration and Measurement Services, and one on Engineering and Related Standards. The committees include leaders in specialized fields, drawn from industry. The purpose of the committees is to aid the Bureau in cooperating with industry in the fields of precision measurement, calibration, and standard practices. William Wildhack, Special Assistant to the NBS Director, is Chairman of both committees.

★ A set of 24 standard metal-organic samples, suitable for spectrographic and chemical analysis of petroleum products, are now available from the National Bureau of Standards. These crystalline, oil-soluble samples are distributed with a certificate of analysis plus directions for preparing a solution of the substance. They can be employed as controls in the determination of metals in crank-case oils, gasolines and other petroleum products.

★ The technical program is now complete for the most comprehensive meeting ever held on the subject of temperature measurement. About 200 papers will cover temperature measurements from absolute zero to 10,000,000 K with interests ranging from the temperature of the human body to the temperature of the sun. Almost every area of the physical, biological, and medical sciences will be represented at the 1961 Symposium on "Temperature, Its Measurement and Control in Science and Industry," to be held in Columbus, Ohio, March 27–31, 1961. The conference is sponsored by the American Institute of Physics, the Instrument Society of America, and the National Bureau of Standards. Persons interested in the symposium may obtain further information by writing to V. W. Sikora, Instrument Society of America, 313 Sixth Ave., Pittsburgh 22, Pennsylvania.

★ An analysis of spectrograms obtained by photographing the planet Jupiter has been completed at the National Bureau of Standards. The first detailed measurements were made of lines in Jupiter's ammonia and methane bands. The presence of the hydrogen molecule was detected from its quadrupole rotation-vibration spectrum. A continuous absorption recorded in the violet and ultraviolet regions closely resembles that of the nitrogen tetroxide molecule. Spectrograms were recorded from 3600 to 8900 A using high-dispersion gratings.

★ The G.E., *Research Laboratory Bulletin* for Summer 1960, reports production of a large piece of pyrolytic graphite. It is hard, dense and silvery-gray. Above 3000 F, it has the highest strength-to-weight ratio of any presently considered material. Above 5000 F, the tensile strength is approximately 40,000 psi.



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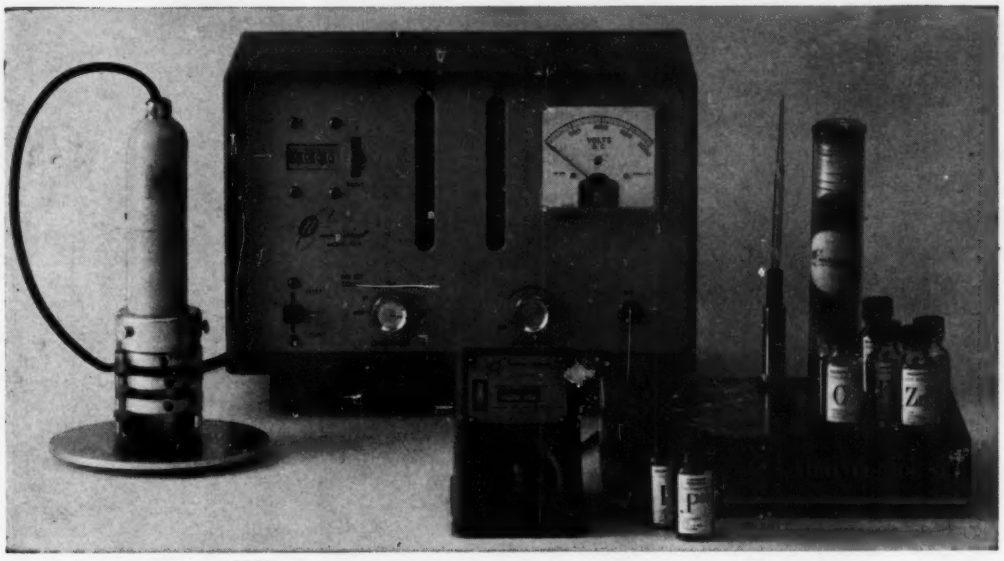

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Chem Ed

EDITORIALLY SPEAKING

The most appropriate first lines of type for a new volume of the JOURNAL OF CHEMICAL EDUCATION should contain greetings and promises to the 1236 new friends who added their names to our subscription list in 1960. This expression of confidence is at the same time the most heartening and humbling statistic among the consistently record-breaking data for Volume 37. The November, 1960, issue went to 12,924 paid subscribers. The 12 issues for 1960 contained 764 pages of editorial material, 15 more than 1959. Several circumstances made possible this bonus bargain for the same four subscription dollars. The phenomenal increase in advertising revenue (57 more pages in 1960 than in 1959) is also an agreeable fact-of-publishing-life! (Readers can best say "Thanks" to the enterprising Mr. Gould by letting advertisers know that they read the JOURNAL ads!)

Prospects for the volume that begins with this issue will, we hope, reflect the confidence that a growing subscription list gives us. Readers can look for features treating such topics as diamond synthesis, nucleogenesis, SAMA, Dexter and other award addresses, and the important "recent advances" symposia sponsored by the Division at national ACS meetings. Geochemistry is scheduled for February, Inorganic for April, Solid State for May, and Organic for June.

We call attention to the new monthly Chem Ed feature, "Chemical Projects," beginning on pages 6–9 of this issue. "Research Ideas for Young Chemists" is the very apt sub-title. The proposal is to focus on the "research" emphasis instead of the "project" aspect which often degenerates into gadgetry and chart-lettering in so many Science Fairs. These will be challenging; perhaps they will appear to be too high a level for the bewildered beginner or the timid teacher. Frankly, the aim is to help raise standards. Nor is the pre-college course for the future chemist the only one that needs standards raised! We hope this series can catalyze what *every* teacher should offer his students: research as an organized attack on a problem for which the answer is not known.

Professor Lewin's Chem Ed feature series on "Chemical Instrumentation" will continue to make each 1961 issue increasingly valuable. The discussion of infrared measurements begun in 1960 will continue for several months. Nuclear instrumentation will be the next topic for three or four issues, followed by an equal number each to be devoted to chromatography and polarography. Preliminary plans are being made to publish in book form sometime this year the material which has appeared in 1959 and 1960.

The value of the JOURNAL OF CHEMICAL EDUCATION to all chemists will be enhanced by two other publications announced in this issue. A Ten Year Cumulative Index covering volumes **26** through **35** will be published next month. Professor Lloyd B. Howell of Wabash College has put prodigious effort into building an index for the working chemistry teacher. Far more than the conventional author and title compilations, this more-than-9000-item listing includes a great variety of cross-referencing and "sub-subject" entries that is the outgrowth of personal experience in using THIS JOURNAL as a "living textbook." A grant from the NSF has underwritten the preparation of this volume to make its break-even price of $2.50 a terrific bargain. Combining this new index with the existing 25-year Cumulative Index makes THIS JOURNAL uniquely useful.

The other 1961 project is the publication of another collection of reprints. (See advertisement on page A57 of this issue.) Although "Supplementary Readings for the Chemical Bond Approach" was compiled as resource material for those engaged in the CBA project, all readers of these pages will recognize the appeal of the article titles. Many modern interpretations of chemical bonding are developed further than usually found in textbooks. The utility of the ideas in these papers is shown by the fact that most of the authors' stocks of reprints have long since been exhausted. This volume fills a real need. (Again at a bargain price, thanks to NSF underwriting of the editorial work.)

We appreciate you 13,000 friends, old and new. We hope you will not be disappointed in 1961.

J. A. Campbell
Harvey Mudd College
Claremont, California

The Chemical Education Materials Study

There are many ways to teach secondary school chemistry, and the chemists that I have talked to feel that chemists should explore several of these ways. This is the reason for the existence of both the Chemical Bond Approach and Chemical Education Materials Study groups, and their interest in working with other experimental programs in chemistry. It will be interesting to see how parallel the developments may be. The intent, however, is not to produce a single, "best" chemistry course. Rather we wish to try out ideas and make it easy for others to adopt and adapt from them. Chemistry courses certainly should, and doubtless will, continue to differ in details. The main purpose of the present studies is to investigate major concepts and emphases, to base a high school course upon them, and to determine the feasibility of the resulting material.

The CHEM Study makes the fundamental assumption, in preparing material, that a student going into high school chemistry already believes firmly that atoms and molecules and nuclei and electrons exist. We assume that these are words the majority of students know and that they have some notion, albeit hazy, of what the words mean. Actually, if their ideas of atoms are hazy, it is all to the good. The best representations of atoms are hazy, and if students start off in this position we have very little to clear up. It is when students have those little dots before their eyes that the difficulties are great.

Having put forward our basic assumption, let me go on and list our operating conditions and some of the ideas we hope the student will have assimilated, and will be able to use by the end of the course.

The Role of Observation

We are convinced that a chemistry course must be based on an experimental approach. In order to emphasize this we have titled our book "Chemistry, An Experimental Science." And we begin the course in the laboratory. The first day the student comes to class he lights a candle and is asked to observe what he sees.

We were concerned lest a candle be treated by the students as a trivial thing, but for most it now appears to be a productive source of observation. The student is asked to write down in five or ten minutes what he observes in the candle. He is then asked to revise his work that evening at home and to bring back to school with him the revised summary of what he has observed about a burning candle. He is not given his text until the second day. In it he finds a three-page appendix called "Description of a Burning Candle" written by a professional chemist. The appendix points out 53 different observations. Most students list between six and twelve. After the description of what a professional chemist sees when he looks at a candle, the appendix goes on as follows:

(a) It (the description) is comprehensive in *qualitative* descriptive terms. Did you include mention of appearance? smell? taste? feel? sound? (Note: a chemist quickly becomes reluctant to taste or smell an unknown chemical. A chemical should be considered to be poisonous unless it is *known* not to be.)

(b) Wherever possible, the description is stated *quantitatively*. This means the question "How much?" is answered; the "quantity" is made more meaningful by the "how much" expression, "bright but not blinding." The statement that heat is emitted might lead a cautious investigator who is lighting a candle for the first time to stand in a concrete blockhouse one hundred yards

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EDITOR'S NOTE: The "Chemical Education Materials Study" is one of two large-scale programs being supported by the National Science Foundation to investigate ways of improving the teaching of chemistry in secondary schools. (The other is the "Chemical Bond Approach." See THIS JOURNAL, **37**, 209 (1960).) CHEM Study began preliminary work in January 1960, and has rapidly progressed to active trial of its first materials. Glenn T. Seaborg is Chairman; J. A. Campbell is Director. G. C. Pimentel (Berkeley) headed the writing conference and L. E. Malm (Utah) led the group preparing laboratory experiments during the summer of 1960. D. W. Ridgway is in charge of film production.

The contributors include Robert F. Campbell, Miramonte H.S., Orinda, Cal.; Saul L. Geffner, Forest Hills H.S., New York; Theodore A. Geissman, UCLA; Melvin Greenstadt, Fairfax H.S., Los Angeles, Cal.; Edward L. Haenisch, Wabash College; C. Robert Hurley, Sacramento State College; Keith MacNab, Sir Francis Drake H.S., San Anselmo, Cal.; Bruce H. Mahan, Univ. of Cal., Berkeley; Margaret Nicholson, Acalanes Union H.S., Lafayette, Cal.; Clyde E. Parrish, Cubberley Senior H. S., Palo Alto, Cal.; Robert W. Parry, Univ. of Mich.; Michell J. Sienko, Cornell; Robert Silber, ACS, Washington, D.C.; Luke E. Steiner, Oberlin; and Robert L. Tellefsen, Napa H.S., Cal.

The first issue of the quarterly *CHEM Study Newsletter* was sent to all high school chemistry teachers on the NSTA list, to members of the Division of Chemical Education of the ACS, and to those who asked to be placed on the permanent mailing list.

Succeeding issues will be sent to those on this permanent mailing list. Readers who wish to receive the *Newsletter* should send a card or letter to CHEM Study, Room 457 West Hall, Harvey Mudd College, Claremont, California.

A limited supply of the trial edition of the text and manual will be available after January 1, 1961. Science supervisors, directors of curriculum studies, or individuals otherwise especially interested in the CHEM Study may request copies of the text and manual. Requests will be filled as long as copies are available.

Various accounts of the project have appeared in the scientific press (see, for example, *C&E News*, October 17, 1960, pp. 100–102). Readers of THIS JOURNAL want more than generalities and promises. Accordingly, the Editor asked Dr. Campbell to prepare this draft of his tape-recorded remarks delivered at the dinner of the Division of Chemical Education held at the New York ACS meeting. The original title was "Radicals and Free Radicals"; its aptness will appear as the reader proceeds.

away. The few words telling him "how much" heat would save him this overprecaution.

(c) The description does not presume the "importance" of an observation. Thus the observation that a burning candle does not emit sound deserves to be mentioned just as much as the observation that it does emit light.

(d) The description does not confuse observations with interpretations. It is an observation that the top of the burning candle is wet with a colorless liquid. It would be an interpretation to state the presumed composition of this liquid.

It seems important, as this last point illustrates, to get the student to distinguish between what he can see and what he thinks it means, even at this first very early stage. During and after some six days of laboratory work, the class continues to discuss the candle at considerable length, going into the various roles of such things as the wick and the fact that one can in a candle isolate an intermediate in a chemical reaction, the soot. Very little soot comes out the top of the candle, yet you can find a great deal of soot within the flame. Thus, we introduce here, in the second week, the concepts of mechanisms of reactions, rates of reactions, energy release and activation energies, phase changes, products of reactions. Indeed, the candle introduces in a clear fashion most of the fundamental ideas of chemistry in terms of a system which the student himself can observe and understand. He also finds out that "simple" systems are not necessarily simple, but that they can be comprehended in simple terms.

The Importance of Laboratory Experiments

Let me briefly cite some of the other laboratory experiments and parts of their purpose. We had a long and very interesting discussion on whether to do the copper-sulfur experiment. Many schools do this and it is one of my favorite experiments. We all wanted to use it. The disagreement was whether we should point out that the product is a non-stoichiometric compound or not. Good experimentalists never get a formula of Cu_2S, and they should not. Is it not, then, a serious mistake to tell a student who has gotten a ratio of 1.9 or 1.8, which is correct, that he should have obtained a ratio of 2 copper to 1 sulfur? And is it correct to confuse an error in the theory with experimental error?

We finally resolved the problem very simply by substituting an experiment in which a copper wire is put in a silver nitrate solution. This is a beautiful experiment, both esthetically and scientifically. One gets quantitative results in good agreement with theory. The student weighs copper wire, places it in a silver nitrate solution, weighs the copper remaining after two days, weighs the silver which forms, and finds the charge on the copper ion and the silver ion, or to be more exact the ratio of the charges, using the atomic weights. We deliberately say little about ions up to this point in the course, so that ions are discovered experimentally by the student.

The students then convert the metallic silver into silver chloride and get the formula of silver chloride. They can also predict the formula of copper chloride. They thus get two experiments for the price of one, and, although silver is fairly expensive, the cost per student is only about five cents. These and all our other quantitative weighing experiments are designed to be done on a triple beam balance costing $20–$28. All are designed to be done to better than 1 or 2% accuracy, (± 0.01 g) sufficiently accurate to give the student a sense of pride in his work.

From this we go on to building space-filling molecular models. These are intended to acquaint the students with bond lengths, bond angles, covalent and van der Waals radii, the relative sizes and shapes of molecules, and the packing behavior of atoms and molecules in crystals and liquids.

Weight relations in chemical reactions, introduced in the silver experiments, are further tied down by letting weighed amounts of lead nitrate and potassium chromate react in aqueous solution. The lead chromate is filtered out and weighed, the water evaporated so that the potassium nitrate may be weighed, and the chemical equation written in terms of moles of materials involved.

The molecular weight of a gas is determined by direct comparison with the weight of an equal volume of oxygen. Rather than concentrating on the temperature and pressure variations, which are normally minor corrections on the major factor of weight, the experiment concentrates on the weight itself. This should add emphasis to Avogadro's Law and its great usefulness. Thus, molecular weights become average relative weights of equal numbers of molecules rather than numbers some have associated with an almost mystic value of 22.4 liters.

The emphasis on quantitative experiments presented in these examples continues throughout the laboratory work. We have also organized the material so that the student, as often as feasible, carries out an experiment in the laboratory before he reads a full discussion of it in the text. He then has a chance to proceed into an unknown region on his own, to make his own discoveries, and then to tie them together with later help from text, friends, and teacher. In other words, he experiments rather than demonstrates.

Geometry and Models

The laboratory and the textual materials stress the importance of the forces acting between atoms and molecules and of the geometric factors affecting their properties. At this point, we rely very heavily on the use of molecular models, primarily space filling models which (in many cases) the student will build. We discuss in some detail the use of models in science, and their limitations. The student realizes atoms are not really made of styrofoam, but it is not necessarily clear that they may not be of the same hardness or that they are not really red, and white, and orange, and blue.

Some Ideas of Major Importance

It is also important to educate students concerning the very large numbers involved in any chemical system, the very large numbers of atoms and molecules and their minute sizes. The conservation laws become much more vivid and useful when tied to this concept. Here we reverse the usual order, and emphasize that chemists normally think, not in terms of the conservation of mass–energy, but in terms of the conservation of atoms and of electrical charge. These two laws are more directly applicable to most chemical situations that the student will meet than the conservation

of mass-energy. Students taught with this emphasis seem to balance chemical equations quickly and intelligently and to approach equilibrium, rate, and mechanism ideas more readily.

The concept of energy and its role in chemical reactions comes in for extensive treatment. A modified Born-Haber treatment is used to interpret many reactions, but still to be explored is the extent to which entropy and free energy should be treated. The CBA is vigorously working on entropy and free energy, but there is little on either in our first edition. We do introduce the idea of randomness and the tendency of systems to become random. Whether we will explore free energies and entropies in a more thorough fashion still remains to be seen.

Kinetics and mechanisms are treated and the concepts used. It seems unfortunate that most introductory courses treat chemical reactions in terms only of the reagents and the products, while completely neglecting the occurrences represented by the arrows or equal signs. Yet the intermediate stages constitute some of the most interesting sections of chemistry. We may, in the future, develop thoroughly some mechanism such as that of the hydrogen-oxygen reaction, pointing out that hydrogen and oxygen do not react directly to give water. Water eventually forms, but there is little evidence that molecular hydrogen and molecular oxygen give water directly.

A discussion of mechanism leads logically to the concept of dynamic equilibria, certainly one of the most important concepts to gain from a chemistry course. These ideas apply not only to chemical systems, but also to historical, economic, and social conditions. As was once pointed out to me when I was extolling the principle of Le Chatelier, Adam Smith discoveerd this principle somewhat before Le Chatelier. He just applied it in terms of economics instead of in terms of chemical systems.

The concept of dynamic equilibria serves as an excellent basis for discussing the competitive factors acting in chemical systems in general. There is always competition between several possible states. The net change depends on the combination of competitive factors acting. Acid-base and redox systems are dealt with on this basis, and, as stated above, we may eventually discuss the energy-entropy competition in some detail.

So far I have not mentioned quantitative treatment of data. I believe it is safe to say that we do not emphasize quantitative treatment so strongly that students with only a year of algebra would fail to handle it. The principal emphasis is placed on using realistic experimental data (e.g., weight data rather than per cent compositions) in carrying out fundamental calculations involving weights, volumes, concentrations, temperatures, and pressures. Equilibrium constants and E°'s are developed and used in a qualitative fashion, but their quantitative applications are treated in "fine print."

In summary, then, let me use different words than I have so far. We would hope that a student when he leaves the course will think of any chemical system with which he comes in contact in terms of the structure of the system. By structure here I mean not only electron structure, but the geometrical arrangement of the atoms, the relative sizes and shapes of the atoms, the packing together of atoms and molecules, the forces between them, and how these affect their chemistry. He will also think in terms of dynamics. He will not only have organized a great deal of factual information, but just as important, he will be able to interpret his own new observations in terms of these concepts of structure and dynamics.

Organization of the Course

The first third of the course gives an overview of chemistry. The second third investigates the major generalizations we think should be covered at the secondary school level. These are: Energy and chemical reactions, rates of chemical reactions, equilibrium and chemical reactions, acids and bases, oxidation-reduction, ionic reactions, stoichiometry, atoms and their structure, periodicity of chemical properties, and electronic structure. All of these are introduced and developed from an experimental point of view. The last third of the course explores chemistry in more detail, building on these generalizations.

Thus, one has the overview first, then the introduction through experiment of the generalizations, and then the use of the generalizations in interpreting larger chemical schemes.

In the last section we include some chemical systems of major, long-term interest to a high school student. For example, there is a discussion of hemoglobin and its mechanism of operation under the general topic of complexes. The relationship between chlorophyll and hemoglobin is developed. A path is prepared for investigating chemical similarities between plants and animals, such as the porphyrin ring structure occurring in both.

This does not mean the student is supposed to memorize the porphyrin ring. In fact, one of our emphases is that the student should not be required to memorize very much. He should tie facts together with concepts, not memorize valences, chemical symbols, or formulas. He is asked to learn facts by using them, rather than by memorizing them for the imminent quiz.

"Radical" or "Different"

The question occasionally comes up, "How radical is the CHEM Study approach?" The answer is, I believe: "Not very radical as far as the chemistry goes." We *are* different from what goes on in the secondary school chemistry now.

At this point I am tempted to play upon words a bit. A radical, as a chemist uses the word, is highly conservative. A chemical radical does not change readily, but proceeds unaltered through many situations. This is an attribute we do not desire. A "free radical" is something else again, and if we must be considered radical, let us be considered "free radicals," highly reactive, causing changes on all sides, but always leading to more interesting products than we started with. The free radicals will react and disappear, but the system will have changed.

Going back to a more typical nomenclature, we do not desire to be radical in our approach to chemistry.

We do think that there are some things that can be improved, and some changes to be tried. Apparently many chemists agree. One of the most encouraging things about the Study so far is the willingness and enthusiasm among those who have been asked to participate on all levels, and the interest which the high schools and their teachers have already shown in the Study.

Let me cite one statistic. Twenty-four teachers were invited to come to Claremont in August and become familiar with the materials. The teachers were to perform all the laboratory experiments and thoroughly discuss the text. They then were to decide whether or not they would use the materials in their classes. It was made clear that their presence in Claremont involved no commitment to use the material, but that if they did use it, they were to adhere closely to it. All 24 decided to use the materials.

Now, I cite this as an interesting statistic only because I want to hasten to add that many of them are skeptical as to how well the materials will succeed. The staff has its doubts too, but criticisms from all concerned are being actively gathered. Staff members are meeting once a week throughout the year with the teachers. In fact, four of the staff are actually teaching the course in two high schools.

The Study is also investigating films (moving, filmstrip, and still), monographs, teacher's guides, lecture experiments, and models, with a view to producing such materials as will enhance the course. Suggestions are actively solicited for staff consideration.

Our long term plans are to produce a tested course by the fall of 1963. It will, by then, be in its 4th or 5th revision. At that time we may have some better idea as to what can be done to make high school courses more effective than they are now.

The over-all aim, then, is to generate and collect ideas which will not so much outline a course, but set a tone and suggest directions in which the first course can move so that it honestly presents a contemporary view of chemistry and its continual growth.

Shirley W. Gaddis
Bethany College
West Virginia

A Simple Filtration Technique for Gravimetric Determinations

Most chemistry teachers recognize the desirability of using more gravimetric experiments in the freshman laboratory. However, if a precipitate is to be separated and weighed, the planning for the experiment presents difficulties. The teacher must feel sure that his students have the skill to carry out the filtration techniques. He must also be sure that there is in his stock room the necessary equipment. This means that a rather expensive inventory of Gooch or sintered-glass crucibles has to be maintained.

This paper offers a method by which the filtration can be done using a simple technique and inexpensive apparatus. The basic idea is this: Two 9-cm Whatman No. 1 filter papers are placed on the balance pans and carefully tared against each other by trimming one paper or the other with scissors. If especially good results are desired, the handling of the papers should be done with tweezers. The papers are folded together to make a single filter. The precipitate is filtered on the top paper of the pair. The precipitate and paper are washed thoroughly and allowed to dry together for one week. The papers are then separated and the top paper with the precipitate on it is weighed using the bottom paper as a tare.

The assumption is that since the two papers are subjected to the same treatment throughout, the change in weight will be the same for both papers. Thus, the weight of the precipitate is the sum of the weights which must be added to the tare pan.

To illustrate the possibilities of this technique, the determination of the per cent silver in a dime has been used. In a private communication, the General Counsel for the Treasury Department states that, in his opinion, it is permissible to destroy *completely* U. S. coinage. This is not the same as illegal defacing of currency.

The dime is cut in half to make a sample which is weighed to ±0.001 g. The sample is reacted with 4 ml of 8 *M* HNO_3 by warming gently. One ml of 18 *M* H_2SO_4 is added to aid the rapid precipitation of the silver as AgCl by 3 ml of 6 *M* HCl. The precipitate is warmed and stirred for 30 min., and the supernate then poured through the 2-paper filter. The precipitate is washed by decantation in the beaker as well as later on the filter until a negative Cl^- test is obtained. The papers and precipitate are dried one week. By using three acetone washes the AgCl can be weighed the next day. The papers are separated and the precipitate weighed as explained above.

To test this method a total of 74 determinations was made over a period of years. Summarizing the results obtained: The highest value obtained in the 74 analyses was 90.2% Ag; the lowest value obtained in the 74 analyses was 89.76% Ag; the mean per cent was 89.92%; (U. S. coin metal is 90% Ag). The R.M.D. of this series of 74 values was 1.4%.

Those teachers who are skeptical of the precision and accuracy possible by using this technique should try it before judging it. It seems pertinent in this context to say that this technique has been used in our sophomore course in quantitative analysis for the gravimetric determinations of the soluble chloride and sulfate. Starting with semimacro samples of 100 mg our students have been reporting results that cannot be distinguished in accuracy and precision from the results obtained by using the customary crucible procedures.

Jay A. Young
King's College
Wilkes-Barre, Pennsylvania
and **John K. Taylor**
National Bureau of Standards
Washington, D. C.

Chemical Projects

Research ideas for young chemists

Many scientists were stimulated toward a career by their own early curiosity about natural phenomena. They began while in high school or even earlier, either building apparatus from materials found around the home or using equipment borrowed from a friendly advisor. In their laboratory work the initial aims were not always successfully achieved nor perhaps were they even clearly in mind, but the activity itself was characterized by two important criteria: The "investigation" was undertaken voluntarily; the "investigator" was curious about some aspect of nature.

Today, many students of high school age and younger are working on science projects; each spring these efforts are publicly exhibited in a "Science Fair." Many of these exhibitors have a sincere interest in their work but others participate because this kind of activity has become socially popular or because their teacher encouraged them to participate (not always without a remark about the effect such cooperation might have upon their grades for the course).

Since neither of the collators of this series of articles is a high school teacher we do not presume to suggest that a student should or should not be strongly urged to generate an artificial interest in the local Science Fair. However, as judges of these exhibits we have often noted that many of the exhibits are more expository than scientific. Some that purport to be scientific fall short of the desirable minimum in demonstrating real understanding on the part of the student, in the quality of the beginner's scientific efforts, and in the thoroughness of the study undertaken.

Because of the particular nature of chemistry, it seems to be more difficult to find a suitable Science Fair project in chemistry than in biology, physics, or possibly even mathematics. Fortunately, many of the articles published in the JOURNAL OF CHEMICAL EDUCATION do contain suggestions, direct or indirect, for further work by interested students. Many of these suggestions are suitable for use by high school students who wish to conduct an investigation and present the results of their work in their local Science Fairs. Other suggestions are similarly useful to freshman students in college chemistry who wish, or who are urged, to undertake an open-end experiment which is a bit more sophisticated than those described in laboratory manuals.

With this in mind, we intend to select material from every branch of chemistry represented in appropriate articles from THIS JOURNAL since its beginning in 1924. These will be presented in abstracted form each month for the use of interested high school and freshman college students of chemistry and their teachers. Limitations of space will often require omission of secondary details; it is intended that the abstracts shall whet the interest of the student, rather than provide complete information. Hence, the abstract will not always convey information sufficient to carry out the appropriate experimental work. In such cases, a place to start would be the original paper. Reference texts and laboratory manuals may also be a first (but not primary) source of information. Obtaining materials and apparatus may also be a part of the "research" involved.

With each abstract we shall append leading questions that indicate some related paths an investigator might study. We hope that a student, under the guidance of his teacher, will select one question from one abstract and pursue the answer as diligently as he can. Since students vary both in their ability and in their interest in the subject, we shall attempt to provide a list of questions of graded difficulty and subject matter for each abstract. The simplest questions will lead the student toward a repetition of the work described in the article itself. Other more difficult questions will lead the student into a study of matters directly related to the topic discussed in the article, but not explicitly included by the original author. The most difficult questions will help the student see relationships between the topic considered in the article and other topics that to a beginner seem unrelated. Some of these more difficult questions will, no doubt, lead the student quickly beyond his depth, and hence will be suitable only for superior students who can accept this kind of challenge. Insofar as possible, we shall try to present the questions at the end of each abstract in order, from simple to complex; but the validity of our estimates of difficulty will in the final analysis necessarily be judged by the teacher and his students.

In each instance, no matter what article or abstract and appended question is selected for further study, our aim will be realized if the beginner achieves a greater understanding of chemistry in particular and of the nature of scientific investigation in general. We believe that a scientist is a scientist because primarily, he is curious about natural phenomena, and secondly, he knows how to proceed in a logical fashion to answer a question that has interested him. Hence, to engender a lasting interest in science, we should help the beginner as early in his education as possible to become aware of

a few interesting questions; we should then help him learn how to answer these questions by a reasonable, logical procedure.

We propose to treat several different topics each month, in successive issues. At the end of a year if the demand seems to warrant, the articles which have been abstracted, along with the leading questions, will be reprinted in one book and made available for distribution. Details of the original articles from which the abstracts have been prepared can be found by locating a library or private collection of the JOURNAL.[1]

Safety Is Important

In work of this kind, safe laboratory practices become paramount in importance. We strongly recommend these minimum precautions: Consistent and regular use of safety goggles and a fire-resistant laboratory apron. (A swatch of material, cut from the hem of the apron, should be tested if this matter is in doubt.) A fire extinguisher and a pail of sand or salt should be available in the immediate area where the work is performed. A fire blanket should be affixed to an adjacent wall. (An old woolen blanket, folded in accordion-fashion, with the folds impaled upon a peg and a rope handle sewn to the outer edge makes a good substitute for the commercial article.) Each step in the student's proposed experimental procedure should be checked *beforehand* by the teacher or advisor. If some of the work is to be performed in a home laboratory, the laboratory should be checked in order to identify and eliminate other safety hazards, such as improperly grounded electrical devices, cloth curtains near a burner, wastebaskets made of combustible material, poor labeling of bottles, etc.

See also the "Laboratory Safety" series of three articles by Mark M. Chamberlain with Gerhardt A. Jabs, THIS JOURNAL, **37,** 446, 511, 583, (1960.)

[1] Should this be impossible for some, and should their number be not too large, full-size photographic reproductions of a desired article can be obtained upon application to one of us (J. A. Y.) when the request is accompanied by 25¢ per page and an addressed, stamped return envelope at least 24 cm × 10 cm.

Keep a Research Record

We also recommend that students be encouraged to keep a notebook in which, with proper citation of the source, they summarize pertinent information learned from their study of reference books, texts, articles in the JOURNAL OF CHEMICAL EDUCATION, and other similar publications. This notebook, together with a laboratory record book, forms an important part of any worthwhile exhibit for a Science Fair. In the laboratory record book, all details of the laboratory work performed should be meticulously and habitually entered at the time the work is performed. Failures as well as successes should be recorded. The pages should be numbered and, as the entries are made, the date should be noted on each page. Incorrect entries should not be erased, but, rather indicated by a single or double line drawn through the entry and initialed to verify the error as a known error. The first few pages, or the last few, of the notebook should be used for a compilation of a list of the contents of the notebook pages, as the pages are filled. (For efficient use, this requires that each page containing entries describing the work be similarly titled in the top margin.) Other details concerning the proper use of a laboratory notebook can be found in many laboratory manuals.

We earnestly solicit the active cooperation and assistance of others who are interested in this work. We would particularly appreciate help in finding suitable articles, in preparing the abstracts for publication, and in composing appropriate leading questions related to the abstracted articles.[2] Suggestions which are used will be credited.

We know of a few published books for beginners which suggest real research investigations in chemistry. We plan to present a list of these soon; since it is quite possible that our knowledge is incomplete, we solicit information about such books from others.

[2] We do not propose at this time to abstract articles from sources other than the JOURNAL OF CHEMICAL EDUCATION. Although other articles may indeed be suitable, limitations of space and copyright problems preclude their consideration at present.

Editor's Note

The first items of the new Chem Ed Feature appears this month on pages 8 and 9. Hereafter it will appear in the section of the magazine bearing page designations A000, as did the "Demonstration Abstracts" during past years.

Projects on related themes will fill each page. The present plan is not to use arbitrary labels designating the area of chemistry involved. Not only would such labels be of questionable value, but they would often be impossible to devise. Two general areas will be involved each month; for example, this issue presents projects related to physical chemistry and organic synthesis and the February themes will be qualitative analysis and physical chemistry.

We very much hope that readers will send us their comments and suggestions. Only thus can this feature become as useful as the authors and editor want.

a Chem Ed feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** Kings College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

The Permeability Method for the Measurement of Surface Areas of Fine Powders

See ALLEN, J. A., AND HAIGH, C. J., *J. Chem. Educ.*, **31**, 354–6 (1954).

The flow of a gas through a porous plug is restricted by the plug, and in flowing through such a plug, the gas decreases in pressure. Measurement of the gas pressures on both sides of the plug, combined with measurement of its length, will yield information about the porosity of the plug. If the plug is prepared by compacting a powdered material in a tube through which the gas is forced to flow, similar data can be used to determine the "average" size of the particles of powder. The experimental details involved in this kind of measurement can be combined in many different ways, each requiring a relatively simple apparatus. In terms of complexity of construction, the method based on Rigden's suggestions is perhaps the simplest.

Air, at a measured pressure, is passed through a plug of powdered material at a measured rate. These data, combined with the measured pressure of the air exiting from the plug, its cross-sectional area and length, the density of the powdered material, and the viscosity of air, provide the information needed to calculate the size of the particles in the plug of powdered material. In general, several determinations of particle size should be made for any one sample of powdered material.

For each determination, the weight of powdered material and the compactness of packing should be different. The results of each determination, on any one substance, are then averaged to give a best value. However, the range of values from which this average is calculated should also be included in any final tabulation of results.

Questions:

Prepare several samples of any suitable insoluble material by varying the conditions of precipitation. These include variations in the concentrations of the two solutions that are mixed, variations in the rate or manner of mixing, inclusion of a third substance, etc. What effect do such variations have upon the size of the precipitated particles? Suggest reasons why the effects you have discovered might occur.

Determine the effect of digestion of a precipitate upon its particle size. Suggest an explanation of this effect and test the validity of your explanation, using other precipitated substances.

Brownian Motion and the Stability of Colloids

See MYSELS, K. J., *J. Chem. Educ.*, **32**, 319 (1955).

A brief calculation shows that only the very smallest of suspended particles can be kept suspended in a liquid medium if the permanence of the suspension is to be attributed solely to Brownian motion. Yet, it is a fact that many many particles much larger than the maximum calculated size do remain in suspension, permanently. This can be attributed to the effect of thermal convection currents within the suspending liquid.

Question:

Prepare a suspension of particles of colloidal size. Calculate the maximum size of particles which can remain suspended permanently if convection currents are eliminated. Devise a suitable method for eliminating these convection currents and for measuring the size of the particles which then still remain in suspension. Compare the results obtained with the calculation you have made.

A Laboratory Experiment in Photometry

See HICKMAN, J. B., *J. Chem. Educ.*, **33**, 560–62 (1956).

Sections of uniformly exposed photographic film are developed for varying lengths of time, and at various temperatures. After fixing, these sections, along with similarly treated unexposed, but developed, film sections, are examined using a microscope and an exposure meter. Measurements of the optical density of the exposed films, thus obtained, are used to describe the characteristics of the film in graphical form.

Questions:

To what extent are the deviations from linearity in the final graphs due to empirical error?

Determine some of the other reasons for deviation from linearity.

In kinetic terms, what is the order of the reaction that takes place in the developer solution?

In this case, is it true that a 10°C rise in temperature doubles the rate of the reaction? If not, is a similar rule applicable? Or, to what extent is the "10°" rule, or a similar rule, inapplicable?

The procedure described by Hickman involves the use of daylight. Carry out the procedure in such a way that the effect of monochromatic (or approximately so) light upon the film can be similarly determined. As an extension of this, study the effect of infrared and ultra violet light.

Prepare your own sensitive film, varying the reagents used, or their proportion, or the manner of mixing them, and determine the effect of these variations upon the properties of the film you have made.

Prepare your own developer solution, varying the composition, and study the effect of these variations upon the measured optical density of the developed film.

(*This investigation sounds so interesting that I would like to do it myself. I hope that students who work on this problem will communicate their results to me.* J. A. Y.)

A Simple Procedure for Preparing Pinacol Hydrate

See WEBER, J. E., AND BOGGS, A. D., *J. Chem. Educ.*, **29**, 363 (1952).

Pinacol hydrate can be prepared by reducing acetone with magnesium, activated with mercury (II) chloride, in benzene, under anhydrous conditions. Weber and Boggs propose a simpler procedure which eliminates the need for benzene and requires only moderate precautions to exclude water.

In the presence of mercury (II) chloride, magnesium reacts with acetone to form magnesium pinacolate. Excess acetone is removed by applying a vacuum (aspirator). A dilute aqueous solution of trisodium phosphate is added to the magnesium salt, forming the desired product, pinacol hydrate, as well as magnesium phosphate (which precipitates) and sodium hydroxide in solution. The mixture is filtered and the product obtained by crystallization at 0°C. The yield varies from 75 to almost 100 per cent.

Questions:

Devise a procedure based upon the method described by Weber and Boggs which will produce a consistently reproducible yield.

Prepare pinacol hydrate by the procedure which requires anhydrous conditions and compare purity of product formed, yield, and simplicity of experimental operations.

Try to devise another modification of the original, anhydrous, procedure which will provide a yield of at least 50% of theoretical. If successful, suggest reasons why your new procedure is successful and test these reasons by further experimental work. If unsuccessful, suggest reasons for your failure and test these reasons.

Will other ketones react similarly?

Can some other metal, instead of magnesium, be used? Can a substitute for mercury (II) chloride be found? If so, suggest reasons why either substitute will work and test these reasons by further experimental investigations.

Continuous Reactors for Preparing Organic Chemicals

See ALLEN, C. F. H., ET AL., *J. Chem. Educ.*, **32**, 394–9 (1955).

Many different procedures for the preparation of reasonably small quantities of organic compounds have been devised and published, notably in laboratory manuals for organic chemistry. In many cases it is possible, by the use of suitable apparatus, to modify these procedures so that the quantities of reagents reacting at any one time are small and the products of the reaction can be continuously removed from the reacting mixture. Allen *et al.* describe the construction and assembly of such an apparatus, with various modifications suitable for several different types of reactions. The components are moderately expensive but, once purchased, will be found useful in many other applications in every modern high school laboratory.

Details for chlorination and esterification are given. Also, the preparation of ethyl benzalmalonate, benzoylacetanilide, palmitoyl chloride, and other compounds are described.

Questions:

By using the apparatus described, prepare a compound related to one of those described by Allen, *et al.* Study the effects of variations in temperature of the columns, in the reaction vessel, etc. upon the yield of product. Or, vary the rate of addition of one or more of the reactants and determine the effect this has upon the yield. Try modifications of your own invention which you think will increase or decrease the yield of product. (Such modifications might include provision for recirculation of reactants, changing the position of a condenser, using a different distilling head, etc.)

Refer to any standard organic chemistry laboratory manual and adapt one of these syntheses to the apparatus described by Allen, *et al.* Vary the conditions, as above, and determine the effect upon the yield of product.

In all cases, purify the product obtained and determine that it is the compound expected. Also, suggest reasons why the variations you have introduced have affected the yield and test your explanations for validity by further experimental work.

The Preparation of Ninhydrin as a Laboratory Experiment

See DOMINGUEZ, X. A., *J. Chem. Educ.*, **30**, 624–5 (1953).

Ninhydrin (triketohydrindene hydrate) is a useful reagent. It is commonly used in paper chromatography to locate, by the formation of a colored product, the position of amino acids on the paper sheet. Its synthesis, starting with phthalic anhydride, is straightforward though it does involve the use of sodium and selenium dioxide. (*The dangers inherent in the use of sodium are well known. Selenium dioxide is more poisonous than many of the more common reagents and should be handled with this fact in mind.*)

Phthalylacetic acid, prepared from phthalic anhydride, is treated with sodium methoxide, thus replacing the oxygen in the five-membered ring with a CH_2 group. After acidification with sulfuric acid, the product, 1,3 diketohydrindanedione, is separated. From this compound ninhydrin is obtained upon heating, in dioxane solution, with a small quantity of selenium dioxide, followed by purification with activated charcoal and recrystallization. The yields of the three steps range from 22.5 to 67 per cent. Various workers have not all obtained the same yields for each step.

Questions:

Is it possible to obtain reproducibly high yields for each step of this synthesis?

Prepare a suitably sized sample of ninhydrin and confirm its synthesis by functional group analysis or by determining the presence of reactive groups in a qualitative way.

By combustion analysis or other suitable means, confirm the fact that you have synthesized ninhydrin.

In addition to its use in paper chromatography, in what other ways can ninhydrin be used? Examine some of these in the laboratory.

Rolf Huisgen
Institute of Organic Chemistry
University of Munich
Germany

Richard Willstätter

From the large number of enthusiasts striving for new knowledge, a few titans arise to guide us to new horizons and uncover new territories of science. These pioneers—with their gift of creative imagination, clarity of thinking, and extraordinary will power—command the attention of the historians of chemistry. "All his ascents are first ascents" was said epigrammatically of Richard Willstätter (Fig. 1) when he was awarded an honorary degree.

Willstätter was born in 1872 in Karlsruhe, which at that time was the residence of the grand duke of Baden. He decided at the age of 12 to become a scientist and at 18, after hearing Adolf v. Baeyer's impressive lectures at the University of Munich, he knew that chemistry would be his future field. Baeyer, who as Liebig's successor contributed so much to the reputation of the Munich laboratory, had begun to grow old at that time and accepted only a limited number of co-workers. It was only after Willstätter had asked the alkaloid chemist Professor Einhorn for a subject for his thesis that Baeyer became aware of the highly gifted young man; Baeyer then looked after him so intensively that Willstätter later considered himself mainly a disciple of Baeyer.

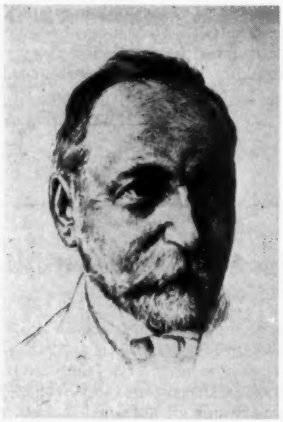


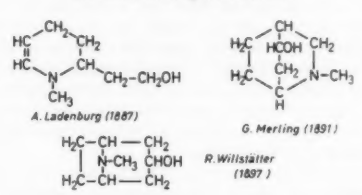
Figure 1. Richard Willstätter (Engraving by P. Halm).

Early Research: Alkaloids

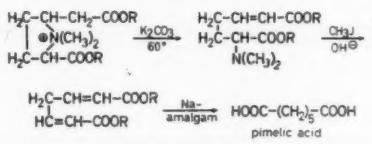
When Willstätter graduated summa cum laude at 22, some results of his thesis struck him as being incompatible with the cocaine structure as proposed by Einhorn in analogy to the formulation of tropine by Ladenburg and Merling. Einhorn was engaged in the synthesis of model compounds showing the anesthetic activity of cocaine. Assuming a wrong structure for cocaine, he discovered the famous local anesthetic novocaine. Einhorn insisted that Willstätter promise not to continue work on cocaine. What was young Willstätter's reaction? He switched to the kindred atropine.

Willstätter, possessed by a "furor experimentalis," within two years carried out the now classical degradations which proved conclusively the structure of tropine. Some transformations which characterize tropine as a derivative of a cyclic unbranched chain of seven carbon atoms are formulated below.

Evolution of tropine formula



Proof of the unbranched carbon skeleton



(R. Willstätter, 1898)

Baeyer requisitioned this brilliant opus immediately for the *habilitation*,[1] the ceremony and process which in Germany mark the beginning of the academic career. Willstätter's determination to dedicate his life to scientific research originated from an incidental observation. The methiodide of tropinic ester, on gentle warming with potash, underwent degradation to the tertiary amine; this anomalously easy Hofmann degradation is a special property of β-aminocarbonyl derivatives.

In his biography, written in exile in 1940, Willstätter disclosed that this observation, though relatively minor, gave him an overpowering feeling of the dis-

Presented as the Carl Schurz Lecture on April 27, 1959, at the University of Wisconsin, Madison, Wisconsin. The author gratefully acknowledges the help of Dr. B. Witkop, Washington, in preparing the English text. The Verlag Chemie kindly gave permission to reproduce pictures from R. Willstätter's biography.

[1] When a green Ph.D. wants to enter an academic career in Germany, he must spend five years in independent research work to demonstrate his capability. Then, after being examined by the faculty, he is "habilitated" and is permitted to lecture.

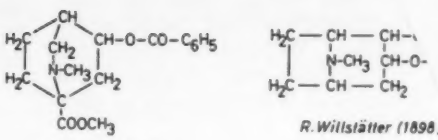
covery of something unprecedented. He regrets that the element of adventure at the outset of scientific investigation cannot carry through to the reader of the eventual complete publication.[2]

The hydrocarbon tropilidene, obtained from tropine by Merling in 1881, was recognized as *cycloheptatriene*. Willstätter not only succeeded in the transformation of cycloheptanone to cycloheptatriene by a clear-cut route, he was able to reintroduce the nitrogen bridge into the molecule and to synthesize tropine by a multistep procedure. The proper conclusions with regard to the structure of cocaine were quickly drawn. The elegant synthesis of ecgonine was carried out two decades later, at which time Willstätter's interest had turned to other subjects. Dioxosuberic ester, prepared by the Kolbe electrolysis procedure, with methylamine yielded pyrrolidine diacetic ester; intramolecular condensation then resulted in the desired ring system.

[2] In this connection I may mention some of Willstätter's philosophical remarks from his autobiography. A purposeful overestimation of the importance of the special problem under investigation helps to supply the needed vigor for the attack. Sometimes, the person too well-read and too critical is unable to adopt this attitude of overestimation. Then the enthusiasm and the driving force for the experimental activity is gone. Willstätter felt that this overestimation of a minor research goal is no longer possible after a great and fundamental discovery has been made. He pointed out that Röntgen, after his discovery of X-rays, was unable to work or publish on minor problems.

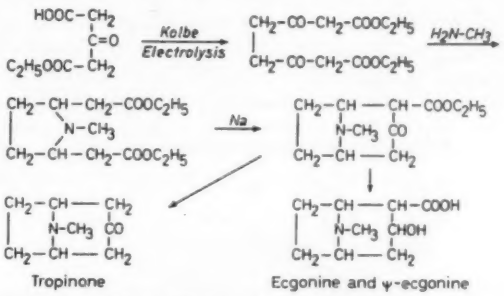
[3] The *extraordinarius* in Germany corresponds roughly to an associate professor, while the German *ordinarius* is the counterpart of the full professor.

Structure of cocaine



A. Einhorn (1893) — R. Willstätter (1898)

Synthesis of e gonine

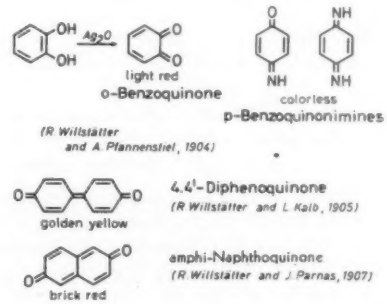


(R. Willstätter, A. Pfannenstiel and M. Bommer, 1918)

Research on Quinones

When Willstätter became professor extraordinarius[3] in 1902, he was faced with the conflict familiar to every chemistry professor: the problem of how to divide his time between teaching and research. He paid due tribute to teaching in lectures and laboratory courses. Willstätter never regarded teaching as secondary; he knew that ingenious *but untrained* students were incapable of great achievements.

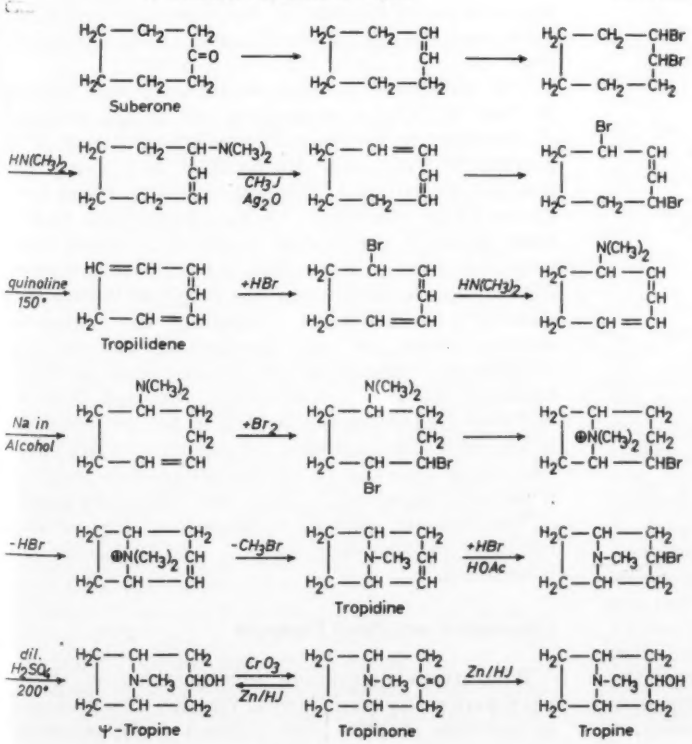
Willstätter's researches on quinones give eloquent testimony of the high educational standard of his co-workers. The red *o*-benzoquinone and its colorless



modification, still unexplained today, as well as the mono- and diimines of *p*-benzoquinones, were all prepared for the first time. The isolation of *amphi*-naphthoquinone was the fruit of three semesters' work. The directions for the preparation of all of these quinones are so short and devoid of any reference to the extraordinary experimental difficulties that unjustified doubts as to their reproducibility were expressed during the first years after publication.

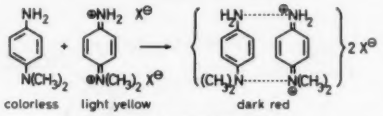
The important elucidation of the character of the Wurster dyes adds to the rich harvest in the quinone field. These red and blue dyes, formed on oxidation of *p*-phenylenediamines, are not quinone-imonium salts,

R. Willstätter's Synthesis of Tropine



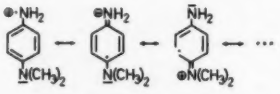
...stätter found these to be only yellow in ... Wurster's Red results from the com...ination of one equivalent each of the benzenoid and quinonoid species. Willstätter's term for this phenomenon was *meriquinonoid principle*. The present interpretation of Wurster's dyes as semiquinones came much later.

Wurster's Red as meriquinonoid salt



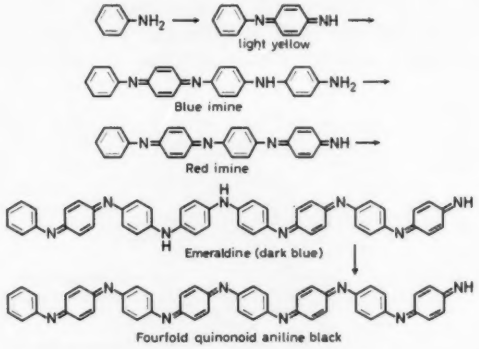
(R. Willstätter and J. Piccard, 1908)

Modern formulation as semiquinonone



Willstätter regarded the clarification of the mechanism of oxidation of aniline to the well-known black dye as his most eminent contribution to aromatic chemistry. "Aniline black" is quantitatively hydrolyzed by acids to *p*-benzoquinone. Today, we should immediately ask the further question whether cations or radicals act as precursors of the dye. Yet, even today, we cannot help admiring the craftsmanship of the master in the separation and structural determination of the 2-, 4- and 8-nuclear anilino-quinones.

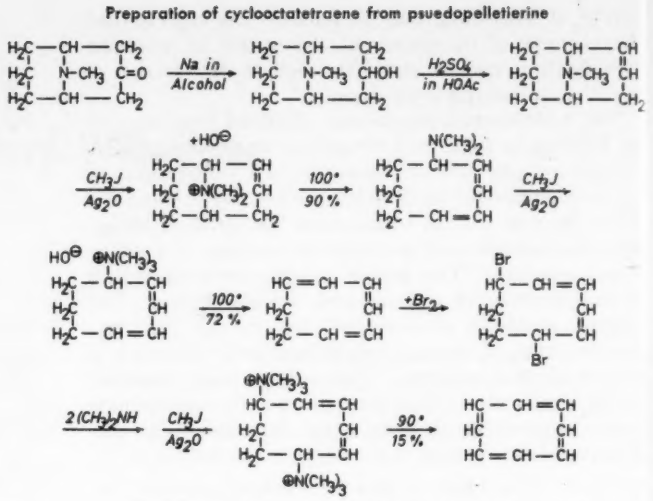
Oxidation of aniline to aniline black



(R. Willstätter, C.W. Moore and S. Dorogi, 1907/1909)

Richard Willstätter never bothered about "small potatoes." With forethought and deliberation he came to grips with the most difficult problems of his time. Johannes Thiele explained the stability of benzene by the compensation of the so-called partial valencies. Willstätter saw in cyclooctatetraene, the higher vinylog of benzene, a suitable model for checking Thiele's hypothesis. In a backbreaking piece of work extending over eight years, the alkaloid pseudopelletierine was transformed to a few grams of the yellow tetraene which, in contrast to benzene, displayed the character of a reactive olefin. The molecular-orbital theory accommodates the observed high reactivity; 8 π-electrons in cyclic conjugation is a violation of the Hückel rule. The valence bond method rationalizes the *non*-aromatic character by the lack of coplanarity.

Preparation of cyclooctatetraene from psuedopelletierine



(R. Willstätter, E. Waser and M. Heidelberger, 1912/13)

In his 1942 biography Willstätter complained that the preparation of the remarkable yellow hydrocarbon had not been repeated for more than a generation, though important physical constants were still lacking. But it so happened that at that very time cyclooctatetraene was being obtained by the tetramerization of acetylene in the Badische Anilin- und Sodafabrik. I suppose that Walter Reppe in 1941 had the first pounds of that yellow hydrocarbon in hand.

Willstätter's endeavors to prepare *cyclobutadiene* as a lower vinylog of benzene failed. This problem remained unsolved for many decades. Finally, in 1959, R. Criegee succeeded in isolating tetramethylcyclobutadiene as its crystalline, deeply colored complex with nickel chloride. C. Nenitzescu isolated in the same year a silver nitrate complex of cyclobutadiene itself.

The birthplace of cyclooctatetraene was Zürich. In 1905 Willstätter accepted a call as full professor of chemistry to the Swiss Polytechnic Institute (Eidgenössische Technische Hochschule) in Zürich. The teaching obligations at this institute at that time were known to be terrifying. Of the predecessors in that chair, Victor Meyer had lost his nerve and Eugen Bamberger his mind. Despite this heavy teaching burden, the six years at Zürich were the height of Willstätter's scientific productivity. Preparing the numerous demonstrations for the introductory lectures was troublesome, but apparently his successors in Zürich lightened this load considerably. Leopold Ruzicka, Willstätter's grandson as it were in the professorship, in his first lecture addressed the audience: "Gentlemen, can you imagine that on mixing two colorless solutions a red color develops?" After the affirmative answer of the students, Ruzicka continued: "Then we need not carry out that experiment." And that is the way it remained.

Chlorophyll and Plant Pigments

Willstätter's magnificent investigations on chlorophyll were partly carried out in Zürich. It was obvious at that time that the green pigment of the plants not

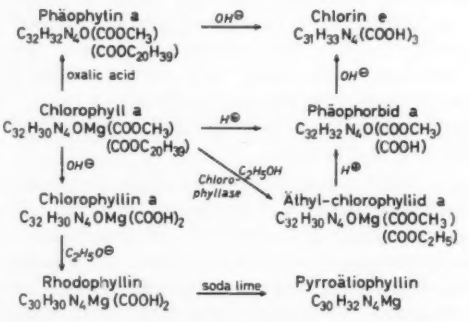
only satisfied man's aesthetic feelings but acted as a photosensitizer in the light-induced reduction of carbon dioxide to carbohydrates, quantitatively the most important organic systhesis on earth. There was nothing in this field on which Willstätter was able to build. The extraordinary sensitivity of the leaf green had led to the most contradictory statements. Willstätter, using refined methods of work-up, was able to isolate from more than 200 plant species one and the same chlorophyll, a mixture of the components *a* and *b* in constant ratio.

Chlorophyll *a*—$C_{55}H_{72}N_4O_5Mg$
Chlorophyll *b*—$C_{55}H_{70}N_4O_6Mg$

A complication in the work-up procedure is worth recounting. The transfer from the test tube to the isolation on a pilot plant scale had been a bit hasty. The Merck Company at Darmstadt extracted huge amounts of spinach in copper kettles with organic solvents. Unfortunately, all of the chlorophyll obtained turned out to be the copper complex.

Willstätter recognized chlorophyll as a magnesium complex from which the metal could be removed by acids. Chlorophyll turned out to be a dicarboxylic acid esterified with methanol and a new unsaturated alcohol phytol. On treatment of plant material with ethanol, the enzyme chlorophyllase catalyzed a transesterification of phytol by ethanol. In the autumn of 1906 Willstätter crystallized ethylchlorophyllide. His biography describes the scene where he poured the pure crystals, sparkling like jewels, on to a plate at the dinner table, letting his young wife share in his pride and delight. In 1907, Willstätter published a paper describing the acid and alkaline degradation of chlorophyll, a paper which he later considered the highlight of his scientific career.

Degradation with acid and alkali



Willstätter learned that the oxygen content of chlorophyll is not involved in the binding of the magnesium. Rhodophyllin, the product of a several-step alkaline degradation, gave on decarboxylation with soda-lime an oxygen-free pyrro-etiophyllin which was still a magnesium complex. He suggested a chelation with the pyrrole nuclei. He knew already of the close relation between leaf green and the red hemoglobin, and he degraded hemin in a similar way to the oxygen-free mother substance etioporphyrin.

Willstätter concluded his investigations on chlorophyll in 1913 with a book "Untersuchungen über Chlorophyll," in collaboration with Arthur Stoll (Fig. 2), who served for many years as president of the International Union of Pure and Applied Chemistry. Chlorophyll still had not given away the secret of its structure. Shortly before, Küster had proposed a structure for hemin, based perhaps mainly on intuition, which afterwards proved to be correct. Willstätter himself preferred a tetrapyrrylethylene structure.

Many scientists have asked why Willstätter, one of the most famous chemists of his time, dropped his work on chlorophyll. The difficulties of isolation had been overcome, and the field was open for chemical investigation. Did he tire of the problem which he had been studying for so many years? Did he consider the spade work complete and the rest of the task as a mopping-up operation to be left to others? I suppose that Willstätter in 1913 was so filled with new problems and plans that he simply had to abandon some old ones. Free from envy, he later appreciated and admired Hans Fischer's brilliant structural elucidation and partial syntheses of chlorophyll.

Figure 2. Arthur Stoll.

On the other hand, the process of *photosynthesis* in the green leaf commanded Willstätter's keen interest. Extensive investigations dealt with the constancy of the photosynthetic coefficient (absorbed CO_2/O_2 set free), the chlorophyll content during photosynthesis, the system chlorophyll and carbon dioxide, the dark (Blackman) reaction of assimilation, and the ratio between chlorophyll content and photosynthetic activity. In 1917, Willstätter published his experiences in book form. Here again foundations were laid for others to come. His search for the intermediates of photosynthesis had not yet been successful. The time and the methods were not ripe for an attack on this problem.

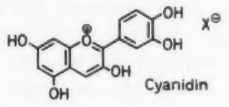
In 1910 the Kaiser Wilhelm Institutes were founded in Germany—free and independent institutes where outstanding scientists, free of all teaching obligations, dedicated themselves to self-chosen problems. In 1911, Willstätter accepted a call as director of the Kaiser Wilhelm Institute of Chemistry, and in 1912 moved to the new building at Berlin-Dahlem. A true friendship soon bound him to his institute neighbor Fritz Haber, the discoverer of important catalytic and electrochemical processes. At the opening of Willstätter's institute, Adolf von Harnack made a classic understatement: "Well-equipped laboratories are essential prerequisites for the progress of chemistry.

Indeed, science is capricious and its progress does not always follow the prefixed river-bed, but often goes its own way. Nevertheless, a well-equipped laboratory saves a great deal of energy."

The larger technical facilities of the institute and the prospects of continuing an investigation on the red and blue pigments of flowers without interruption had attracted Willstätter to Berlin. The crystallization of the blue dye of the bachelor's button or cornflower was a success of his last year at Zürich. Starting material had been dried bachelor's buttons ordered from the Merck Company. In Berlin Willstätter not only brought fresh plants into the laboratory but he also cultivated the various flowers. In the summer after Willstätter's arrival the institute was surrounded by gorgeous fields of blossoming flowers: Double bachelor's buttons, scarlet dahlias, large-petaled asters, red sage, violet pansies, and bronze-colored chrysanthemums.

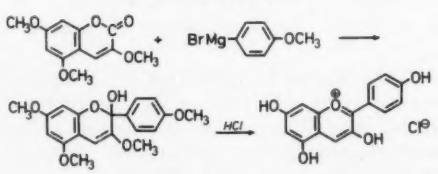
The double purplish cornflowers contained up to 14% of their dry weight of the dye cyanin, a glycoside split by acids into 2 moles of glucose and the aglycon cyanidin. The blue sodium salt of cyanidin was dissolved in acids with a color change to red. Willstätter's surprise is not hard to visualize; such a behavior points to a basic function in an nitrogen-free dye! In the red solution he recognized an oxonium salt derived from a hydroxychromane. Was it not a breath-taking discovery when Willstätter, on harvesting his flower fields in the fall, found the same *cyanidin* as coloring matter in the red rose, certain dahlias, the red poppy, and somewhat later in the colors of cherries, plums, cranberries, and elderberries? Nature's grandiose palette of red and blue hues and shades had been reduced to a few closely related structural types, of which cyanidin is the most widespread. Willstätter found that subtle variations in *p*H were mainly responsible for the multitude of shades in the flower garden. The proportions of the red oxonium salt, the violet phenol, and the blue phenoxide anion change with the hydrogen ion concentration.

Chromophore of the colouring matter of roses, corn flowers, dahlias, poppies, cherries and cranberries



Cyanidin

Synthesis of pelargonidin



(R. Willstätter and L. Zechmeister, 1914.)

Two years later the outbreak of the first world war brought this investigation to a close. In August, 1914, all co-workers were drafted. The crop of flowers was carried in large baskets to the military hospitals. Shortly before, Zechmeister, now professor at the California Institute of Technology, had completed the synthesis of pelargonidin. Willstätter never resumed this work, which was masterfully continued and completed after the war by Sir Robert Robinson.

The Swedish Academy awarded Willstätter the Nobel prize of 1915 for his research on plant pigments. The diploma was trimmed with ornaments of green leaves, blue bachelor's buttons, and scarlet geraniums.

A small piece of applied military research is connected with Willstätter's name. At the outbreak of chemical warfare there were no protective or defensive measures on either side. Perhaps it is not well known that the gas-mask is an invention of Fritz Haber and Richard Willstätter. More precisely, Willstätter's contribution was the construction of a cartridge containing mainly charcoal and hexamethylenetetramine which absorbed chlorine and phosgene from the incoming air. Not only were the German gas-masks equipped with such filters, but the Allied Forces analyzed captured gas-masks and soon hexamethylenetetramine was found in every filter.

In 1915 Willstätter received honoring calls to chairs in Göttingen, Vienna, and Munich. A cordial letter from his old teacher Baeyer strengthened him in his resolution to return to Munich where the foundation of his scientific career had been laid. The Bavarian Minister had promised to begin with the urgently needed enlargement of the laboratory despite wartime conditions. The building of a new lecture hall seating 600 people was to replace Liebig's old auditorium, but it was not completed until 1920.

Enzyme Chemistry

It was an admirable venture that Willstätter, despite the lack of co-workers and the terrible wartime conditions, should attack the biggest and toughest problem: the nature of enzymes and their mode of action. In 1911 he had begun investigating peroxidase and catalase, two enzymes that destroy hydrogen peroxide. The isolation work which was started in the Zürich laboratory was now resumed on a broad basis. Soon similar investigations were started on carbohydrases, proteinases, and lipases.

The enrichment of enzymes by adsorption techniques can be traced back to Willstätter. The difficulties in obtaining reproducible activities of adsorbants stimulated fundamental studies on metal hydroxides and hydrogels. These were courageous forays into inorganic fields. Free silicic acid supposedly should not exist; the text books maintained that instead, hydrosols of silicon dioxide are obtained. Willstätter proved the transient existence of the monomeric ortho acid, H_4SiO_4, which is capable of permeating plant membranes and seems to be responsible for the silicification of wood.

The results of ten years' hard work were collected in a book in 1928. The "Untersuchungen über Enzyme" was published jointly by Willstätter and his excellent collaborators Wolfgang Grassmann, Heinrich Kraut, Richard Kuhn, and Ernst Waldschmidt-Leitz. No fewer than 43 additional names are listed as coworkers. A later generation tended to criticize repeatedly the outcome of the enzyme work as generally unsatisfactory. It is true that the rather lengthy enzyme adsorption methods did not become standard

methods of the biochemical laboratory. Nevertheless, the first successful separations of carbohydrases and peptidases were made possible in this way. Willstätter enriched horse-radish peroxidase by a factor of 12,000 and the invertase of yeast 3500-fold. He did not have the good fortune to obtain a crystalline enzyme. In retrospect, Willstätter's selection of enzymes was not an auspicious one. Invertase from yeast, for example, so far has defied all attempts at crystallization.

Enzyme chemistry owes to Willstätter a significant impetus. He inaugurated *in vitro* reduction by fermenting yeast as a laboratory technique. The reduction of chloral and bromal yielded the corresponding carbinols. The tribromoethanol known under the trade mark "Avertin" came into wide usage as a rectal anaesthetic. A renowned English physician considered the drug as being "one of the most beneficial aids to relieve human suffering we know of at the present time."

Dark clouds overshadowed Willstätter's time in Munich. Perhaps I have been paying more attention so far to his work than to his personal fate. After 5 years of happy marriage, his young wife died in 1906. He never married again. He gave his son and his daughter a careful education. In 1915 he lost his son as a consequence of a serious illness.

Let us go back further into the past: Willstätter's youth, spent at Karlsruhe and Nuremberg, was somewhat overshadowed by his Jewish origin. A. v. Baeyer recommended christening to the young lecturer as a means of avoiding obstacles in his academic career. Christening at that time removed the barriers erected by society. A. v. Baeyer, himself of Jewish origin on his mother's side and distantly related to Heinrich Heine, advocated the principle of assimilation. Willstätter's pride refused such an action. Not at all an orthodox Jew, he preferred like many other scientists to be free from religious and confessional ties.

Early Retirement

In the summer of 1924 the Munich faculty had to look for a successor of the famous crystallographer and mineralogist Paul Groth. Groth himself proposed passionately Viktor M. Goldschmidt in Oslo, the founder of modern geochemistry. Goldschmidt was a Jew. At the instigation of some members the Faculty refused consent, giving way to the pressure of the street, as it were. That very same day Willstätter tendered his resignation. Demonstrations of sympathy from the students, the faculty, the university, and the ministry of education did not change the tragic decision of the 53-year-old Willstätter. His final official action in the faculty was the suggestion and appointment of the highly esteemed Heinrich Wieland as his successor (Fig. 3).

After his self-imposed retirement in September of 1925, Willstätter never set foot into the institute again. He declined brilliant offers from domestic and foreign universities, including three in the United States. Wieland installed a special laboratory for Willstätter's co-workers, who were thus enabled to finish their doctoral or habilitation theses. Until 1938 Margarete Rohdewald continued her investigations on the metabolism of sugar in muscle. Daily she reported the newest results to Willstatter, who retained his residence in Munich.

Willstätter's foresight of things to come proved to be correct. He was not born a fighter to stem the rising tide of intolerance in political life. He retired and maintained his contacts with good friends. Hardly had Hitler seized power when discrimination against the Jews found expression in vicious pogroms. The dreadful aspects of these persecutions are well known. The German universities were forced to dismiss Jewish professors. In 1936, Carl Bosch, Director of the Badische Anilin-und Sodafabrik, warned Hitler of the set-backs in chemistry and physics as a consequence of these dismissals. The fanatic's answer: "Then we have to get along without chemistry and physics in the next 100 years."

Figure 3. Heinrich Wieland.

In 1938 Willstätter saw his hope vanish of spending his remaining years in his home in Munich. After a month-long martyrdom he succeeded, with the help of his true friend Arthur Stoll, in obtaining an emigration visa for Switzerland. Only a small part of his belongings and art treasures could be saved. The great old man spent the last three years of his life in Muralto near Locarno. From his home, Villa Eremitaggio, he enjoyed the wonderful view of the Lago Maggiore. Here he found time to rest and write his autobiographical sketches. On the 3rd of August, 1942, he died of cardiac failure.

During the war and Nazi regime, the German chemists were allowed neither to hold memorial lectures nor to publish obituaries for Richard Willstätter. In 1956, a worthy tombstone and memorial was erected, not in his homeland but in the country of his last refuge. A black marble stone at Muralto tells of a rich and well-filled life. Besides the symbols of wisdom and some alchemical instruments, leaves, fruits, grapes, and a fermentation vat remind us of his research.

Willstätter's biography "Aus meinem Leben" was edited by Arthur Stoll and published by the Verlag Chemie. In an epilogue added by Stoll, the mere enumeration of the honors and awards bestowed upon the great scientist requires the space of three pages. Let me conclude the lecture with Willstätter's words on the occasion of the Award of the Willard-Gibbs Medal in Chicago in 1933: "Our experiments are not carried out to decide whether we are right, but to gain new knowledge. It is for knowledge's sake that we plow and sow."

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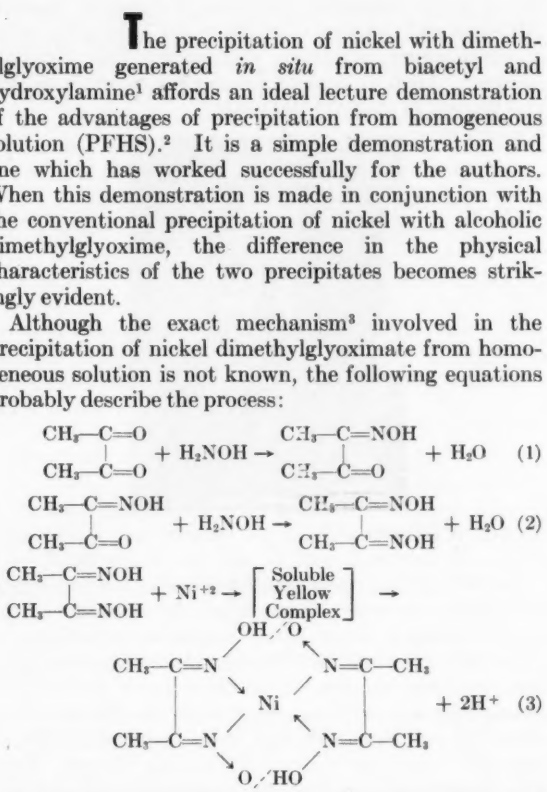
Precipitation from Homogeneous Solution

A lecture demonstration

The precipitation of nickel with dimethylglyoxime generated *in situ* from biacetyl and hydroxylamine[1] affords an ideal lecture demonstration of the advantages of precipitation from homogeneous solution (PFHS).[2] It is a simple demonstration and one which has worked successfully for the authors. When this demonstration is made in conjunction with the conventional precipitation of nickel with alcoholic dimethylglyoxime, the difference in the physical characteristics of the two precipitates becomes strikingly evident.

Although the exact mechanism[3] involved in the precipitation of nickel dimethylglyoxime from homogeneous solution is not known, the following equations probably describe the process:



When the appropriate reagent solutions are first mixed, the resulting solution is virtually colorless. The solution begins to turn *yellow* apparently as the result of complex formation between nickel and dimethylglyoxime (reaction 3). The solution becomes increasingly more yellow and subsequently long *red* needles of the nickel chelate begin to appear in about five minutes. In the conventional procedure, precipitation occurs too rapidly to permit visual observation of the yellow complex except under certain conditions.[4]

If, from the start, a light beam is passed through the homogeneous solution, both the development of the yellow color and the formation of the precipitate are readily observed. The nickel dimethylglyoximate crystals precipitated from homogeneous solution exhibit a slightly different reddish hue than those obtained by conventional precipitation.

The Experiment

Solution A: Five g of ammonium chloride, 3.0 g of hydroxylamine hydrochloride, and 80 mg of Ni^{+2} are dissolved in enough distilled water to bring the volume to about 200 ml. The *p*H of the solution is adjusted to 7.5 with ammonium hydroxide and the final volume is brought to 400 ml with distilled water.

Solution B: Exactly 0.60 g purified biacetyl (Burdick and Jackson Laboratories, Muskegon, Michigan) is dissolved in enough distilled water to bring the total volume to 400 ml.

Solution C: Five g of ammonium chloride, 5 ml of concentrated ammonium hydroxide, and 80 mg of Ni^{+2} are dissolved in distilled water to a 400 ml volume.

Solution D: Forty ml. of a one per cent solution of dimethylglyoxime in ethyl alcohol are added to sufficient 1:1 ethyl alcohol-distilled water solution to bring the total volume to 400 ml.

Conventional Precipitation: Pour Solution C into a one liter beaker. Add Solution *D* to Solution *C* with stirring to produce the voluminous nickel dimethylglyoximate.

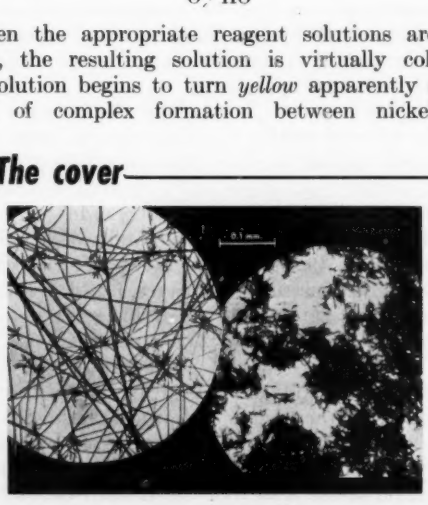
Precipitation from Homogeneous Solution: Pour Solution *A* into a one liter beaker. Add Solution *B* with stirring. In a few minutes crystals of nickel dimethylglyoximate begin to precipitate which will slowly grow several millimeters in length.

It is possible to adjust the *p*H of Solution *A* so that the precipitation from homogeneous solution will begin in almost any desired amount of time. An approximate guide is:

*p*H	Time of Start of Precipitation, Min.
7.9	2
7.7	4
7.5	6
7.3	8
7.1	12

The difference in the physical characteristics of the two precipitates will become even more apparent upon filtration.

The cover



The contrasting appearance of nickel dimethylglyoximate precipitates is shown by a pair of photomicrographs. The sample pictured at the left was precipitated from homogeneous solution as described in the text. The one shown at the right was obtained by conventional methods.

The authors wish to acknowledge the partial assistance of the Atomic Energy Commission under Contract AT(11-1)-582.

[1] Salesin, E. D., and Gordon, L., *Talanta*, **5**, 81 (1960).

[2] Gordon, L., Salutsky, M. L., and Willard, H. H., "Precipitation from Homogeneous Solution," John Wiley and Sons, Inc., New York, **1959**.

[3] Salesin, E. D., and Gordon, L., research in progress.

[4] Diehl, H., "The Applications of the Dioximes to Analytical Chemistry," The G. Frederick Smith Chemical Co., Columbus, Ohio, **1940**, p. 13.

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Deionized Water by Electrodialysis

A great deal of attention is being given to the use of electrodialysis in the preparation of potable water from brackish water because of the interest being shown in this area by the U. S. Department of the Interior, Office of Saline Water. Not much attention has been given, however, to the use of electrodialysis in the preparation of deionized water, equivalent in quality to distilled water. Yet this is the area in which the method potentially is most efficient.

If we wish to prepare distilled water, the amount of energy required is practically independent of the salt content of the original water. Thus it costs about the same to distill sea water as it does to distill pure Rocky Mountain spring water. The energy cost for converting water to steam is calculated to be:

E = 540 cal/g × 1 g/cm³ × 3785 cm³/gal. × 1000 gal. × 1.16 × 10^{-6} kw hr/cal = 2400 kw hr/1000 gal.

Even if we recover part of this energy by using the incoming stream to cool the condenser, it is estimated that the minimum energy requirements might still be several hundred kilowatt hours per thousand gallons.

To arrive at the basic minimum energy cost for separating water and salt in a saline solution, it is helpful to consider the separation to be carried out by a process which we might call reverse osmosis. Suppose we have a very large tank (1,000,000 gal. capacity) of sea water, and suppose this tank has one wall consisting of an osmotic membrane. If the tank were also equipped with an imaginary piston which could sweep through a volume of 1000 gal., then we could theoretically exert enough pressure on the piston to cause water to pass out of the tank through the osmotic membrane. This pressure would have to be slightly greater than the osmotic pressure of the saline solution. The osmotic pressure of sea water is about 335 psi. We may then calculate the work done in causing the piston to sweep through a volume of 1000 gal. at 335 psi:

w = 335 psi × 1000 gals. × 68,947 dynes/cm²/psi × 3785 cm³/gal. × 2.78 × 10^{-14} kw hr/erg = 2.4 kw hr/1000 gal.

This basic minimum energy requirement for removing the water from the salt in sea water is thus roughly a tenth of 1% of the energy required to convert water into steam and about 1% of the energy required in a multiple effect distillation process.

Many years ago van't Hoff pointed out that the osmotic pressure, π, is proportional to the concentration of the solute, C:

$$\pi = CRT$$

Thus the lower the salt concentration the lower the osmotic pressure and the lower the basic minimum energy required to separate solute and water. However, in order to take advantage of this basic minimum energy we must use some method of separation other than distillation. Methods have been developed using membranes through which salt can be caused to move under the impulse of an electric field.

In 1940, Kurt H. Meyer[1] described the effects of passing an electric current across selective membranes. His suggestions for both the single three-compartment cell and the multiple-cell electrodialysis apparatus are the basis of most of the equipment in use today. The development of such equipment was delayed until the 1950's because suitable selective membranes were not available. Such ion-exchange membrane materials are now commercially available at a cost of a few dollars per square foot.

The Cells in Use

Starting in 1957, we built several electrodialysis cells of the type described by Meyer using Permutit cation and anion exchange membranes No. 3142 and No. 3148. It occurred to us that, since the basic minimum energy requirement in such an electrodialysis cell decreases with the salt concentration, such a cell might be very efficient for the production of deionized water. We designed a cell (Fig. 1) to produce deionized water at the same rate as the usual laboratory still, about 2 gal./hr. Thirty compartments were provided, each about 1 cm thick and 156 cm² in internal cross sectional area. One can calculate from average ionic mobilities at the voltage gradients used (about

[1] Meyer, Kurt H., *Helv. Chim. Acta*, **23**, 795–800 (1940).

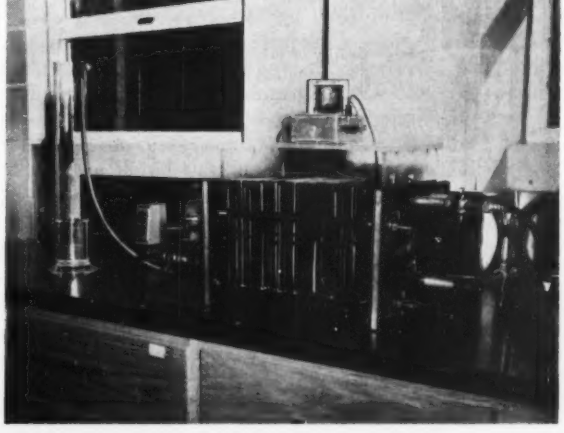

Figure 1.

Presented before the Division of Industrial and Engineering Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

10 v/cm) that approximately 2 min. would be required to deionize one compartment one cm thick. The water would remain about 15 minutes in the cell at a flow rate of 2 gal./hr. The thicker cells were designed to hold a larger volume of water with the idea that the cell might act as its own storage tank and eliminate the necessity for an additional tank for storage. The cell constructed can indeed be operated in such a manner, as will be described later under operation at slug flow.

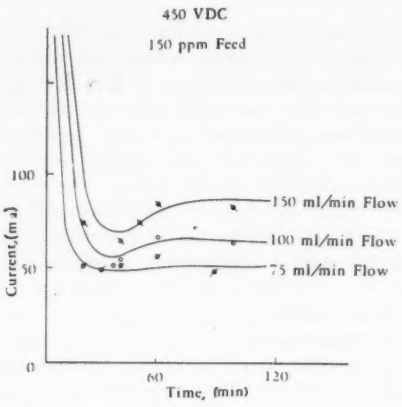

Figure 2.

Water is brought into the cell at normal line pressure of approximately 75 psi. The Permutit membrane is a fabric reinforced membrane and no difficulty has been experienced with rupturing of the unsupported membrane at these pressures. The inflowing stream of water, containing 150–200 ppm total solids, is divided into two streams which flow through alternate cells in series. One stream becomes depleted, the other enriched. The enriched stream also carries away the gas formed at the electrodes, so that there are just two exit streams similar to an ordinary water still. The enriched stream may be discarded in the ordinary manner by which the effluent stream from a still is discarded. We use a stainless steel cathode and a carbon anode. For supplying the dc voltage we have constructed several transformer-isolated, silicon diode rectifiers supplying from 200 to 450 v dc at up to 200 ma across the cell which measures 40 cm between electrodes (Fig. 1).

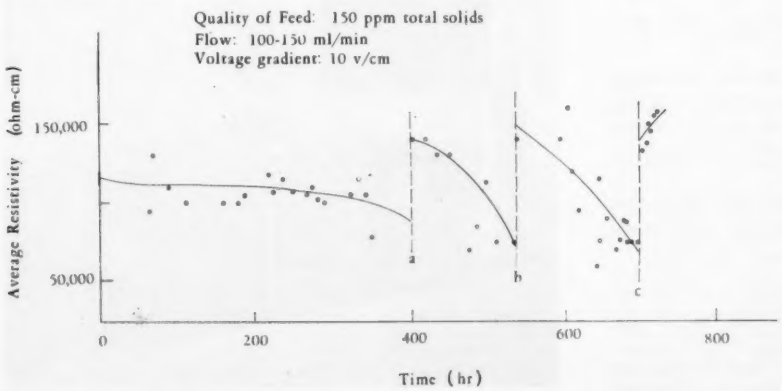

Figure 4.

A typical plot of current passing through cell as a function of time for several flow rates at 450 v is shown in Figure 2. The 150-ppm feed water filled the whole cell when the voltage was applied at time zero in each case. We can see that the depleted stream drops to the equilibrium value within 15 to 30 min depending on the flow rate.

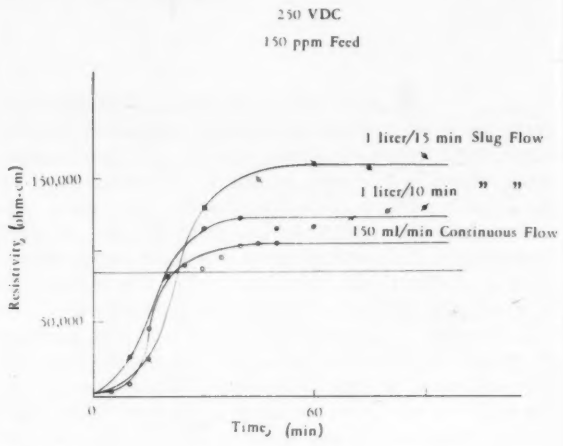

Figure 3.

Perhaps a more significant record is that shown in Figure 3, where the resistivity of the depleted stream is plotted against time for various flow rates at 250 v dc. Here two examples of slug flow are given, one in which depleted water was withdrawn at a rate of 1 l/10 min., another at a rate of 1 l/15 min.

The US Pharmacopoeia (11th Rev., **1936,** p. 65) defines *aqua destillata* as water which "shall not contain more than 5 ppm total solids." If the dissolved solids are all ionic material, such water should have a resistivity of about 85,000 ohm-cm. The straight horizontal line in Figure 3 represents this value of 85,000 ohm-cm resistivity, and thus the arbitrary standard we chose to call "distilled water."

The current required by the cell operating at 250 v dc and a flow rate of 150 ml/min. (2.4 gal/hr) is approximately 50 ma. This is a power consumption of 12.5 watts. An electric still of the same rated capacity for producing distilled water uses 5000 watts or more. Furthermore a still wastes much energy because its high operating temperature causes much heat to be lost to its surroundings, whereas the electrodialysis cell operates at room temperature.

The performance of the cell over a prolonged period of operation is recorded in Figure 4. At points *a* and *b*, the cathode was removed and scoured clean. At point *c*, 2 *N* hydrochloric acid was introduced into the cell for 30 min. to remove scale throughout the whole cell.

At this writing, the cell has been operating for another 150 hr since Figure 4 was drawn, and the resistivity of the depleted effluent is now in excess of 100,000 ohm-cm. Operation for 950 hr at 2 gal./hr flow rate

has produced 1900 gallons of deionized water. Since the feed water contained 150 ppm of solids, at least three pounds of salt have been transported through the membranes in less than one year's operation. The original set of membranes are still in use, and scale removal over the whole cell has been required only once in nearly 1000 hours of operation. Figure 1 shows the cell in operation.

Summary

We believe that an electrodialysis cell can compete with a still for producing "distilled water" for the following reasons:

(1) The cell produces deionized water equivalent in quality to distilled water at a power consumption rate several hundred times less than that of a still of similar capacity.

(2) The cell operates at room temperature.

(3) The cell can act as its own storage tank for limited quantities.

(4) Scale removal is less of a problem than for a still, since much of the salt removed from the water is carried away in the waste stream.

Blueprints describing construction of the cell (Fig. 1) in detail and a wiring diagram for the power supply are available from the author on request.

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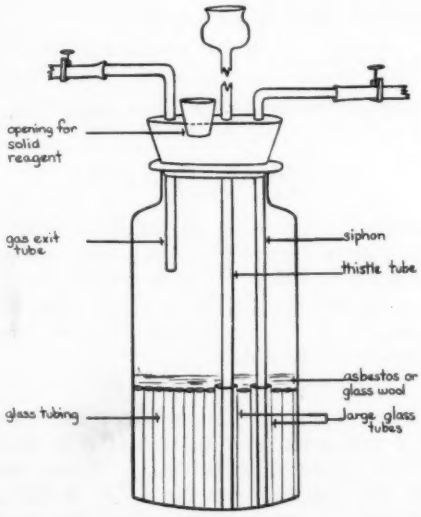
An Improved Gas Generator for Elementary Chemistry

A small-scale adaptation of the Lassieur generator[1] has been developed. This generator combines the economy and easy construction of the wash-bottle type and the efficiency and flexibility of the Kipp. It provides self-controlled evolution of gas from solid and liquid reagents, with reserve gas storage capacity. Generation of hydrogen from mossy zinc and acid, and hydrogen sulfide from iron sulfide and acid, are intended uses.



The generator vessel is a wide-mouth bottle. Pieces of upright 5-mm glass tubing of uniform length are fitted tightly into its bottom. Two sections of larger diameter tubing should be in proper location to accommodate the ends of the thistle tube and siphon.

A heavy layer of glass wool or asbestos is laid over the top of the platform made by the pieces of glass tubing. This forms a stage for the reactive solid and prohibits small pieces of the solid reagent's falling between, or through, the upright tubing. The area below this porous platform serves as a reservoir for the liquid reagent.

The figure indicates the other features of the apparatus such as the means of adding solid or liquid reagents, the gas delivery tube and the siphon for removing spent reagent from the bottom of the bottle.

The operation of the generator is simple. The solid reagent is placed on the porous stage. Liquid reagent is poured into the thistle tube and allowed to fill the volume in and around the platform tubes to reach a level where it starts reacting with the solid. The gas exit tube remains open until air is driven from the system; it is then clamped. The gas pressure builds up until the liquid reagent is forced to a level below the solid. This is possible because of the relatively large reservoir of the acid in the bottle, for the level in the container is lowered little while that in the thistle tube rises sufficiently to balance internal pressure. Therefore, a supply of the required gas is available by merely releasing the pinch clamp on the gas exit tube, which allows the liquid to rise to a level where it once again reacts with the solid.

Waste products accumulate in the solution at the bottom of the bottle. The siphon is then started by pinching off the gas exit tube, opening the siphon, and building up gas pressure until acid is forced through this exit. The siphon continues to operate until the majority of the waste is taken off.

Fresh solid can be introduced through the small stoppered hole as required. The generator is therefore capable of almost continuous operation.

[1] HALL, W. T., *Chem. Abstr.*, vol. 42, page 2478[8].

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Textbook Errors, 28

The Shape of the 2p and Related Orbitals

Many recent textbooks include diagrams of atomic and molecular orbitals. Most of the texts which do this mistake graphs of the angular variation of the $2p$ and related wave functions for actual geometrical descriptions of these orbitals.[1] The result is a distorted and illogical picture of the orbital.

The formula for the wave function, ψ, for a $2p$ orbital may be written as follows[2] in polar coordinates (*1*):

$$\psi(r, \phi) = \left(\frac{k^5}{\pi}\right)^{1/2} e^{-kr}\, r \cos\phi \qquad (1)$$

where the wave function $\psi(r, \phi)$ may be considered for our purpose as being the square root of the probability of finding the electron at the coordinates (r, ϕ), k is one half the effective nuclear charge, r is the distance from the nucleus expressed in units of Bohr radii (0.53 Å), and ϕ is the angle between r and an axis. Any axis may be chosen. p-Orbitals at axes which are at right angles to each other are orthogonal (i.e., noninterfering), so that the three Cartesian axes provide a complete set of orthogonal $2p$ orbitals.

It is sometimes convenient to consider ψ as being made up of radial and angular components, $e^{-kr}r$ and $\cos\phi$, respectively. We may then express ψ either as a function of the distance at a constant angle or as a function of the angle at a constant distance:

$$\psi(r)_\phi = Ae^{-kr}r \qquad (2)$$

$$\psi(\phi)_r = R\cos\phi \qquad (3)$$

where A and R are expressions whose values are given by equation (1). A graph of equation (2) is sketched in Figure 1 and shows how ψ varies radially in any given direction from the nucleus. A graph of equation (3) is the familiar cosine curve, which in a polar graph (*2*, *3*) is two circles tangent at the origin. It is this polar graph which is commonly represented as being the $2p$ orbital. In three dimensions, the graph is two tangent spheres. Sometimes the spheres are given fuzzy outlines, which is not very meaningful. Such graphs show precisely the angular variation of the orbital and should not be used to picture the orbital itself.[3]

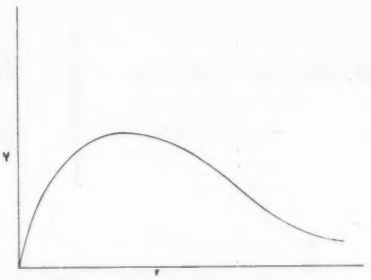

Figure 1. Graph showing radial variation of ψ_{2p}.

To describe the shape of the orbital, one would need to draw a contour line, i.e., a line following a path of constant ψ. To do this, equation (1) may be transformed into Cartesian coordinates by use of $r\cos\phi = x$ and $r = (x^2 + y^2 + z^2)^{1/2}$, where the X-axis is taken as the axis from which the angle ϕ is measured. This yields the formula for the $2p_x$ orbital (formulas for the $2p_y$ and $2p_z$ orbitals are analogous):

$$\psi(x, y, z) = \left(\frac{k^5}{\pi}\right)^{1/2} xe^{-k\sqrt{x^2 + y^2 + z^2}} \qquad (4)$$

Now a contour line in the XY plane can be drawn by setting $z = 0$ and solving for y:

$$y = \left[\left(\frac{1}{k}\ln\frac{k^{5/2}x}{\pi^{1/2}\psi}\right)^2 - x^2\right]^{1/2} \qquad (5)$$

This equation is somewhat simplified by expressing ψ in terms of percentage of ψ_{max}. ψ_{max} may be found by differentiating equation (4) with respect to x where $y = z = 0$, and setting $d\psi/dx = 0$. The value so found, $\psi_{max} = k^{3/2}\pi^{-1/2}e^{-1}$, may then be combined with equation (5) to yield:

$$y = [(k^{-1}\ln\beta^{-1}kex)^2 - x^2]^{1/2} \qquad (6)$$

where $\beta = \psi/\psi_{max}$. Contour lines are shown in Figures 2 and 3 for $\beta = 0.316$ and $\beta = 0.10$ (i.e., $\psi = 0.316\psi_{max}$ and $\psi = 0.10\psi_{max}$). These lines are therefore also the contours for $\psi^2 = 0.10\psi^2_{max}$ and $\psi^2 = 0.01\psi^2_{max}$, respectively.[4] The dots show the

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Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

[2] The formula is written in different forms in many sources The form used here is that of Coulson (*1*), although he uses $C/2$ for k, where C is the effective nuclear charge.

[3] The earliest use of these graphs is probably Pauling's (*2*, *3*). However, Pauling explicitly states that these graphs do not actually show the shape of the orbital.

[4] The notion that equation (3) or its polar graph represents the $2p$ orbital has led to the apparently widespread belief that the contours for ψ^2 must be different (narrower) from those for ψ. This conclusion results because $R^2\cos^2\phi$ is a different curve from $R\cos\phi$, if R is held constant. A more thorough analysis, however, considers the variation in R, and it must conclude that if ψ is constant along a contour line, then ψ^2 must also be constant.

positions of the maxima. The value chosen for k was 1.625, half the estimated effective nuclear charge for a $2p$ electron of carbon (*4*). The probability that the electron may be found within a contour is not given by the above figures but may be calculated by integrating ψ^2 over the volume enclosed by the contour.

The shape of a $2p$ orbital may therefore roughly be described as two *separated* spheres, ellipsoids, or distorted ellipsoids, in increasing order of precision. However, the orbital should not be described as two *tangent* lobes of any kind since that leads directly to the following logical impasse:

First: ψ must equal zero everywhere on the node and it must not be zero any place else;

Second: ψ is constant and finite along a line showing the shape of the orbital (i.e., a contour line);

Therefore, if the finite, non-zero contour lines for the two lobes meet at the node, then at the point of contact ψ must be both zero and not zero at the same time.

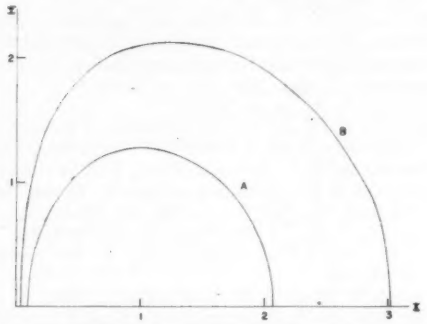

Figure 2. Contour lines for the $2p_x$ orbital in one quadrant of the *XY*-plane. Curve *A* is the contour for $\psi = 0.316\,\psi_{max}$ and $\psi^2 = 0.10\,\psi^2{}_{max}$; curve *B* is the contour for $\psi = 0.10\,\psi_{max}$ and $\psi^2 = 0.01\,\psi^2{}_{max}$. Units are Bohr radii.

As a bonus to the correct understanding of the wave function, it becomes easy to show that the shape of the charge cloud, or the probability distribution, for two orthogonal $2p$ orbitals is not something like a four-leaf clover but rather is something like a doughnut, a cross-section of which is Figure 3. This is especially useful in showing the cylindrical symmetry of the triple bond. The following paragraph summarizes this picture in a non-rigorous manner.

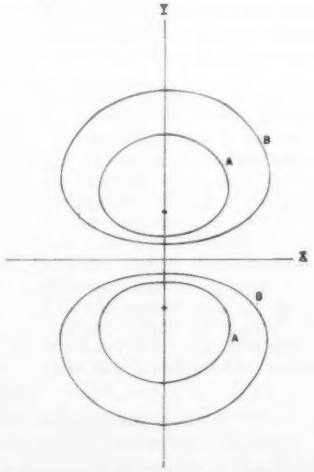

Figure 3. Contour lines for the $2p_y$ orbital in the *XY*-plane. The $2p_y$ orbital may be developed from this by rotation about the *Y*-axis. Contours for total ψ^2 for the $2p_y$ and $2p_z$ orbitals may be developed by rotation about the *X*-axis.

For a $2p$ orbital, the angular variation in ψ is given by equation (3), and therefore $\psi^2(\phi), = R^2 \cos^2 \phi$. For a second $2p$ orbital disposed at right angles to the first, the angular variation in the plane of the two axes, in terms of the angle ϕ at the first axis, is $\psi_{90°}(\phi), = R \cos(\phi + 90°) = \pm R \sin \phi$, and $\psi^2{}_{90°}(\phi), = R^2 \sin^2 \phi$. Therefore the sum of the angular variations of ψ^2 in the plane of the two axes is $R^2 \cos^2 \phi + R^2 \sin^2 \phi = R^2$, which is constant at any fixed distance from the nucleus but which varies radially according to equation (2).

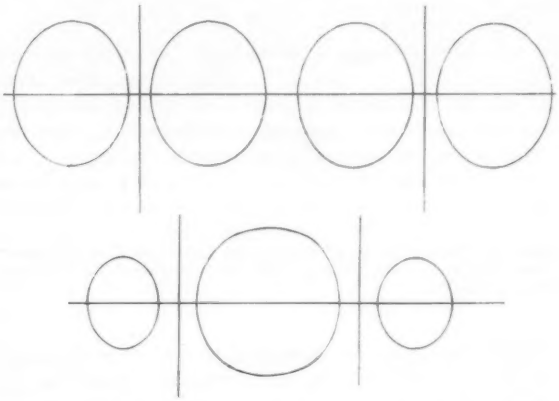

Figure 4. Axial approach of $2p$ orbitals (above), and a $\sigma(2p)$ bond (below).

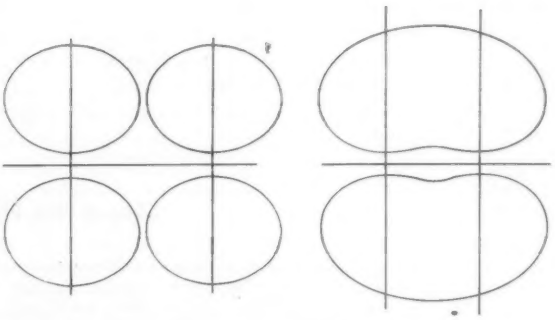

Figure 5. Parallel approach of $2p$ orbitals (left), and a $\pi(2p)$ bond (right).

With the aid of these corrected orbital contours, one can form much better pictures of the covalent bonds derived from the $2p$ orbitals. Figures 4 and 5 show the overlapping of $2p$ orbitals to form a $\sigma(2p)$ and a $\pi(2p)$ orbital, respectively. The π portion of a triple bond (which may be thought of as a σ bond and two $\pi(2p)$ bonds) is sketched in Figure 6.

An improved presentation of the sp^3 orbital is perhaps even more important for the organic chemist. Elementary texts show this variously as an off-center ellipsoid, two unequal lobes tangent at the center, or two unequal lobes separated with a node at the center. While there is an improvement in the above sequence, a calculation of the contour lines shows that none of these is correct. Figure 7 clearly shows that the node is a curved surface which passes between the center and the more extended lobe (*5*).

There are several available references which offer discussions of these orbital shapes, though most of

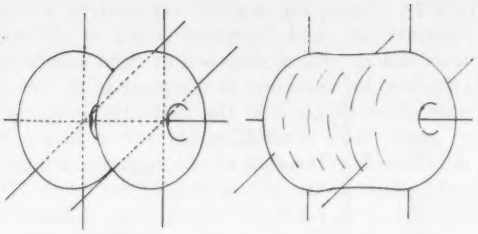

Figure 6. Two pairs of orthogonal 2p orbitals ($2p_y + 2p_z$) at left and their π-bond at right (as in a triple bond).

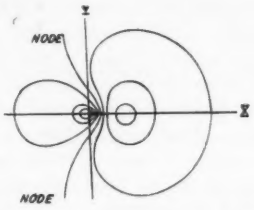

Figure 7. Contours for an sp^3 orbital, after COULSON, C. A., "Valence," Oxford University Press, 1952, p. 190, with permission of The Clarendon Press, Oxford.

them are in highly mathematical terms. The diagrams in (*6*) and (*7*) and the photographic simulations in (*8*) are very helpful, as are the more limited discussions and drawings in (*9*), (*10*), and (*11*). The contour line equations (5) and (6), however, have not yet been observed any place by this writer.

The above analysis shows clearly that the shape of a 2p orbital is quite different from the picture usually given, which is at best a polar graph of the angular variation alone. The correct shape of the orbital can be simply derived in terms of equation (6) and presented graphically through contour lines. This leads not only to an improved understanding of double and triple bonds but also to a corrected picture of the sp^3 hybrid orbital.

Acknowledgment

This paper was prepared with invaluable assistance from Professor Karol J. Mysels, who offered many suggestions and corrections, and Donald R. Lavin, Youngstown University, who prepared the drawings.

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There *Are* Electrons in Atoms!

It is important to give students the real and convincing proof that atoms contain electrons. The evidence provided by most elementary textbooks is the emission of electrons by metals in vacuum discharge and in photoelectric and thermionic effects. Does the emission of electrons by rather drastic conditions really prove the presence of electrons in atoms? Such an argument is like the conclusion that there is smoke in a gun before a shot because it is evolved from the barrel after the shot. Let us remember that a few decades ago it was assumed that the emission of electrons in radioactive decay proves the presence of electrons in atomic nuclei. We now know that this assumption was wrong.

Phenomena do exist which prove unequivocally that electrons are not only emitted from atoms but really are contained in them. The Zeeman effect is an example of such direct evidence. I have found the following discussion to be effective: First, I remind the students that electromagnetic waves (such as those used in radio and television communication) are generated by the displacement of electrical charges and that light waves are the same type of electromagnetic vibrations differing only in frequency (or wave length). Then I remind them that all elementary substances and compounds of an element emit light of characteristic frequency or frequencies. This unique property for each kind of atom means that the same kind of displacement of electrical charge must take place. After that I describe the Zeeman effect and point out that a magnetic field changes the conditions of displacement of electrical charges. Then I show that, according to the laws of electrodynamics, the observed displacement of the frequency and the magnitude of the magnetic field allow one to calculate the ratio of charge to mass (e/m) of the charged particle within the atom which is moving to generate the light. The fact that this ratio turns out to be identical with that calculated for free electrons by other methods is convincing proof that electrons are indeed within the atom.

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Stereoisomerism of Carbon Compounds

In the early stages of a science or of a particular branch of science, many concepts are necessarily of a pragmatic or operational nature. As the science develops there is a tendency for these concepts to be placed on a broader and more theoretical or abstract basis. For example, an early definition of "element" was "a simple material that cannot be broken down into simpler materials." The beginnings of a change in this concept may be seen in Mendeleev's prediction of then unknown elements and their properties. After further development of the atomic theory and Rutherford's discovery of transmutation, the definition given above was changed by the addition of the phrase "by ordinary chemical means." The more modern definition is: "An element is a kind of matter all of whose atoms have the same atomic number" (*1*). This is based on fundamental concepts and does not depend on someone's ability (or lack of it) to decompose certain species of matter.

Some chemists still use concepts and definitions in the field of stereochemistry which are operational in nature, and there seems to be considerable confusion on the subject not only in relatively recent textbooks of organic chemistry but in more advanced writings on stereochemistry. The purpose of the present discussion is to suggest a different setting for the classification of the various types of stereoisomerism commonly encountered in organic chemistry, with the view to providing a better correlation with presently used concepts of atomic and molecular structure. Based upon the models of organic structures which have developed from molecular orbital theory, emphasis is placed on the theoretical chemical significance of the models while the topological aspects, i.e., the presence or absence of symmetry or the nature of the dissymmetry, are considered to be secondary.

First of all, for purposes of this discussion, the traditional distinction between structural isomerism and stereoisomerism should be reaffirmed, clearly limiting consideration to the relationships among compounds having the same structure. "Structure" here refers to the order in which the atoms in a molecule are bonded to each other, and has no geometrical significance even though this may be implied by the way structural formulas are commonly written (*2*). Stereoisomers (though literally "solid isomers") may be defined as compounds having the same molecular structure but with the atoms in the molecule differing in their geometrical arrangement with respect to each other. These two types of isomerism are in a sense independent of each other, but one may consider stereoisomerism as being superimposed on structural isomerism, thus increasing the total number of isomers possible for a given molecular formula.

Stereoisomerism is commonly considered to be of two types, optical and geometrical. Optical isomerism is due to molecular asymmetry which may result from one or more tetrahedral atoms with four different groups attached, or may result from restricted rotation within the molecule. The statement "Isomerism depending on restricted rotation about a carbon-carbon bond is known as geometrical isomerism" (*3*) is hardly satisfactory for it does not exclude many examples normally included in optical isomerism. It is generally recognized that optical isomers cannot be defined as stereoisomers which exhibit optical activity yet the writer of one modern textbook uses optical activity as the criterion in the following way (*4*): "Geometrical isomers may be defined most conveniently as a set of stereoisomers no member of which is optically active." This is an operational approach which depends upon our ability to detect the activity. Aside from any objections to such a definition on theoretical grounds, there is the practical problem of the proper classification of compounds that may be asymmetric but whose optical rotations are so close to zero that detection is unsatisfactory or impossible. (Furthermore, optical activity depends on conditions, such as temperature or wave length, and a compound optically active at one temperature might be inactive at another.)

Before going on to state and interpret his own definition, Wheland indicates the difficulty as follows:

> In view of the vagueness which thus generally attends the terms "optical" and "geometrical" isomerism, a consideration of the meanings of these terms is desirable here. Such a consideration is made rather difficult, however, by the fact that no complete agreement exists among chemists as to exactly where the dividing line between the two types of stereoisomerism is to be drawn . . .It is therefore clearly impossible for any definition of optical and geometrical isomerism to lead to a classification of stereoisomers in complete agreement with the usage of all chemists (*5*).

The confusion and overlapping in the classification of the isomerism of such compounds as the cyclohexane-1,2-dicarboxylic acids is indicated by Wheland at this point. In spite of this pessimism, and after a discussion of "dissymmetry" he offers a definition (*6*): "Geometrical isomers can now be defined as stereoisomers which do not differ in the configuration of any dissymmetric grouping." Whether "in complete agreement with the usage of all chemists" or not, this is a rather unequivocal definition. But it is based on topological relationships and is not closely related to the structural concepts of the molecular orbital model.

"Conformation" is another term in common use that

is subject to some ambiguity if not actual confusion. Some authors treat the subject under the general heading of stereo*chemistry* but in a manner which implies that it is not a type of stereo*isomerism*. Some definitions of geometrical isomerism are so broad that conformations seem to be included as merely one type of geometrical isomers. At the other extreme, conformation is sometimes defined so broadly that all types of stereoisomers might fall within the meaning of the term (*7*). As an intermediate example, well known chemists in the field have stated that

> By conformation is meant any arrangement in space of the atoms of a molecule that can arise by rotation about a single bond and that is capable of finite existence (*8*).

This clearly includes cases of both optical and geometrical isomers—for example, some of the substituted biphenyls and terphenyls, respectively. But in the discussions of conformational analysis and the heights of energy barriers, these polyphenyl compounds, and other optical or geometrical isomers of this type, are commonly ignored. The authors quoted above also make the following statement:

> Conformations (as defined here) constitute definite chemical species which, however, are not separable by presently available methods (*9*).

In other words, a chemical individual of this type when first isolated immediately ceases to be a "conformation" and becomes an isomer. This is not in conflict with their previously quoted statement but places a restriction on the definition that is definitely operational in nature, and is in this respect reminiscent of the older definitions of an element.

A Suggested Classification

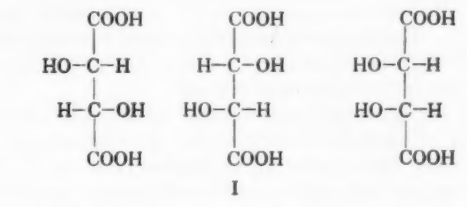
To avoid some of these shortcomings in the traditional division into optical and geometrical isomerism (with conformation still groping for a place in the scheme), and at the same time to relate the classification more closely to the molecular orbital model, a different approach is suggested. Stereoisomers are placed in two general divisions with the distinction based on the type of change that some part of the structure undergoes in converting one isomer into another. Only the type of change which the model undergoes, not the chemist's ability to cause or prevent the change in an actual compound, is of concern here.

One of these divisions is called "inversional" isomerism. *Inversional isomers are stereoisomers which are formally interconvertible only by inversion of one or more carbon atoms with the breaking of one or more sigma bonds and the formation of a corresponding number of sigma bonds.* This might involve the back side attack associated with the Walden inversion or the transitional trivalent carbon atom associated with some racemizations. (This assumes that the inversion does not take place as proposed by Werner (*10*) to explain racemization.)

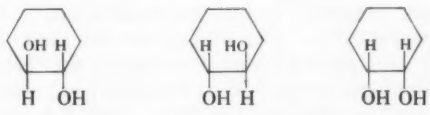
The second main division is called "rotational" isomerism. *Rotational isomers are stereoisomers which are formally interconvertible by the rotation of one part of the molecule with respect to the rest of the molecule about a sigma bond as the axis of rotation without the necessity of disrupting and reforming sigma bonds.* (It is important to note that a *sigma* bond, not a single bond, is referred to here and thus the definition includes the "forced rotation" of the conventional double bond, which in terms of the molecular orbital model involves a change in the overlapping of *p* orbitals as the rotation about the *sigma* bond takes place.) Such transformations *may* be made by breaking and making *sigma* bonds, but the distinguishing feature here is that, formally, rotation is sufficient and *sigma* bonds need not be involved directly. Each of these divisions, inversional isomerism and rotational isomerism, will be considered in turn for illustration and clarification.

Examples of "Inversional" Isomerism

Many of the classical examples of stereoisomers come under the heading of inversional isomerism. For instance, the lactic acids, the tartaric acids and the many aldohexoses are of this type. But also included are the stereoisomeric disubstituted cycloalkanes which may or may not have asymmetric carbon atoms present in the molecule. The isomerism of the 1,2-dihydroxycyclohexanes and of the 1,4-dihydroxycyclohexanes are included in the same classification, instead of calling the former optical isomers and the latter geometrical isomers. Similarities become more evident among compounds like the tartaric acids (I) and the 1,2-dihydroxycyclohexanes (II), in comparison with the similarities of the monomethyl esters of the tartaric acids (III) and the 1,2-dihydroxy-3,3-dimethylcyclohexanes (IV).



I



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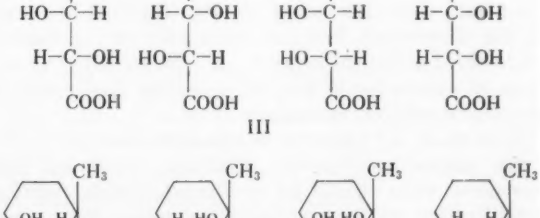
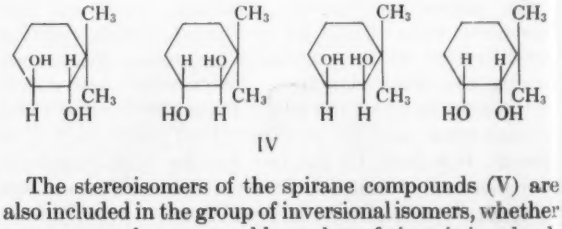


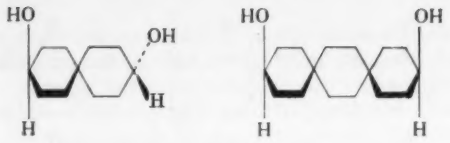
III



IV

The stereoisomers of the spirane compounds (V) are also included in the group of inversional isomers, whether an even number or an odd number of rings is involved, thus placing structures that are similar chemically in the same group.

One feature is common to all of the sets of isomers mentioned. In all cases the transformation of a structure from one stereoisomer to another must involve the



V

disruption and formation of *sigma* bonds, resulting in the inversion of one or more carbon atoms.

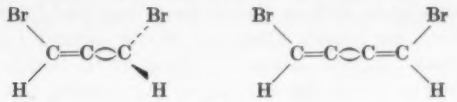
Examples of "Rotational" Isomerism

As indicated previously, the other principal type of stereoisomerism, rotational isomerism, concerns isomers whose interconversion does not necessarily involve the disruption of *sigma* bonds, but rather may take place by the rotation of one part of the molecule with respect to the rest of the molecule about a *sigma* bond as the axis. This is the type of isomer whose isolation has depended upon the degree to which this rotation is restricted under the experimental conditions involved in the isolation. The major causes of restricted rotation are restriction due to *pi* bond hindrance, restriction due to non-bonded hindrance, and restriction due to *sigma* bond hindrance. In some cases only one of these causes may be operating while in others more than one may contribute, but usually one of them predominates.

Inversional isomerism and rotational isomerism, as types of stereoisomerism, are superimposed on structural isomerism. In a similar manner rotational isomerism is superimposed on inversional isomerism. For example, in biphenyl systems the existence of isomers resulting from restricted rotation is independent of any inversional isomerism in either part of the molecule alone, but if such is present it merely increases the total number of stereoisomers possible. However this is not an overlapping of classification in the sense used by Wheland in the case of the cyclohexane-1,2-dicarboxylic acids any more than structural and stereoisomerism are overlapping classifications. The different geometrical arrangements of the atoms which distinguish the molecules of inversional isomers will be referred to as "configurations," while the different arrangements giving rise to rotational isomers will be called "conformations."

Pi Bond Hindrance

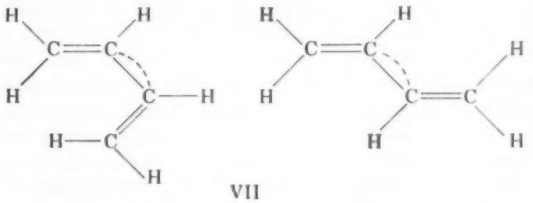
Among the compounds which serve as examples of rotational isomerism, the first to be isolated were the substituted ethylenes, and the existence of such isomers was attributed to the restricted rotation of the double bond. However, the double bond may be looked upon as being made up of one *sigma* bond with the restricted rotation resulting from the overlapping of the *p* orbitals to form the *pi* bond. This overlapping usually constitutes a sufficient barrier to rotation to make it possible to isolate the isomers at room temperature. This constitutes one of the three classes of rotational isomerism, designated as rotational isomerism due to *pi* bond hindrance. The sterecisomeric compounds of the allene type (VI) belong to this same class of rotational isomers whether there is an even or an odd number of cumulative double bonds; again, structures that are similar chemically are in the same group rather than being divided into two groups on the basis of relationships that are not primarily chemical in nature.



VI

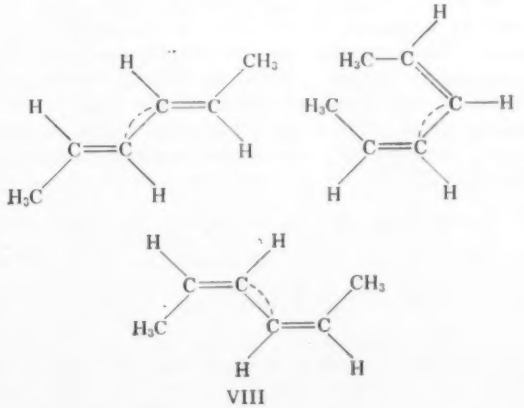
It is of interest to note that while in the case of the usual double bond there is an sp^2 hybridization of the carbon orbitals giving the three coplanar *sigma* bonds, in the case of the middle carbon of an allene system there is *sp* hybridization and two linear *sigma* bonds. The *sigma* bonds are then made up of overlapping sp-sp^2 orbitals, and the planes of the two *pi* bonds are at right angles to each other, intersecting on the line of the two *sigma* bonds. This is the axis about which rotation is considered to occur in transforming one compound into its isomer.

Conjugated systems present an interesting situation which falls naturally into an extension of the rotational isomer concept. In 1,3-butadiene, for example, the overlapping of the *p* orbitals between the second and third carbon atoms would be expected to cause some restriction of rotation. The molecule is considered to be essentially planar and to have a resonanace energy of about 3 to $3^1/_2$ kcal per mole. Although the *cis* and *trans* isomers are not capable of isolation at room temperature with present techniques, we may well assume that they actually represent preferred arrangements (VII).



VII

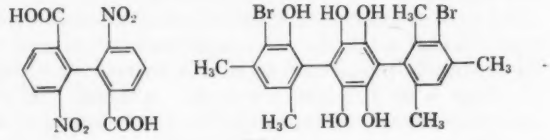
The application of this idea to 2,4-hexadiene indicates the possibility of six isomers. The *trans-trans-trans* isomer (the staggered chain arrangement often depicted) would probably be the most stable; the *cis-cis-cis* isomer the least stable (due largely to methyl group interactions); and the *cis-trans-cis* isomer of intermediate stability. These three of the six possible conformations are shown (VIII).



VIII

Non-Bonded Hindrance

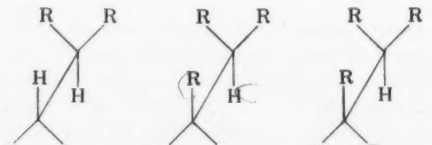
Compounds such as the ortho substituted biphenyls are the best known examples of the second type of rotational isomers, those resulting from non-bonded hindrance. Here the tendency of overlapping *p* orbitals to cause coplanarity of the two benzene rings (a necessary condition for resonance interaction between them) is overshadowed by the so-called steric hindrance of the groups in the ortho positions when these groups are sufficiently large. Again it should be pointed out that these compounds are placed in this class whether they are optically active (as in the case of certain biphenyl and polyphenyl compounds with an even number of rings) or optically inactive (as in the case of some terphenyl and polyphenyl compounds with an odd number of rings). Thus (like the allenes or the spiranes) compounds which are similar in structure and chemical nature are not divided into separate classifications merely on the basis of the presence or absence of symmetry. For each structure shown (IX) two conformations are possible (*11*, *12*).



IX

It has been recognized that in a sense each molecule with an infinitesimal difference in the angle between the planes of the two benzene rings might be considered as a different isomer. This, of course, would mean an infinity of isomers. Actually, this aspect has been ignored in the literature to a large extent and all molecules with angles in the whole range of positions between two energy barriers have been considered as one isomer. Thus those molecules with the same configuration and whose conformations correspond to positions between adjacent maxima of the potential energy curve constitute a single rotational isomer. This viewpoint has been adopted for the present discussion.

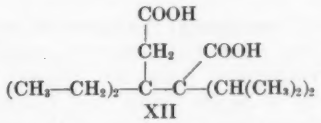
In recent years considerable attention has been given to the study of ethane and some of its derivatives in what has come to be known as "conformational analysis." Since the existence of these conformations is due to essentially the same situation as the existence of the biphenyl type of stereoisomer, these variations of the ethane derivatives (and thus similar variations of all saturated aliphatic compounds) also may be classed as rotational isomers due to non-bonded hindrance. For example, consider a compound such as *sym*-tetra-butylethane. Assuming sufficient hindrance to rotation, this structure would exist in three stereoisomeric forms. These are represented below in perspective formulas (X) and in the Newman projection formulas (XI).



X

XI

It would be of interest to synthesize, if possible, a compound such as 2,2-diisopropyl-3,3-diethylglutaric acid (XII). The syntheses of other glutaric acid



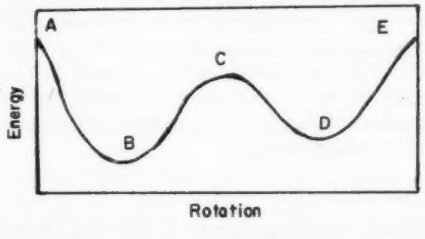
XII

homologs with increasingly larger groups in the 2 and 3 positions might then be attempted. While the carboxyl groups are in the *trans* position no cyclic anhydride can form, but in either of the skew arrangements the anhydride would be expected to form. This might provide a means of separating and isolating the *trans* form from the other two.

In the case of ethane derivatives having the same set of three different groups attached to each carbon (as in the tartaric acids) there are three conformations for each of the three configurations, making a total of nine stereoisomers. When the asymmetric carbon atoms are dissimilar twelve stereoisomers are possible.

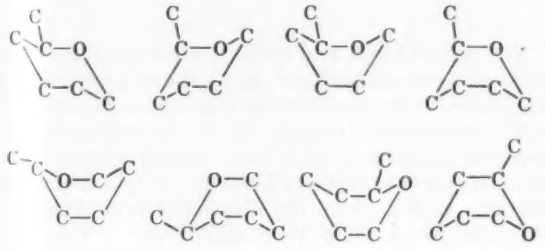
Sigma Bond Hindrance

The conformations of cyclohexane and its derivatives exemplify the third class of rotational isomerism, that due to *sigma* bond hindrance of rotation. In many cases non-bonded hindrance is also involved. Considering the figure as a generalized potential energy diagram of the cyclohexane system, the minima at *B* and *D* represent the chair and boat forms. In all



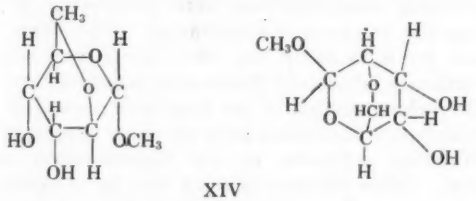
cases the barrier at *A* would be due almost completely to *sigma* bond hindrance—that is, the resistance to extreme deformation of the tetrahedral carbon bonds and the eventual rupture of the ring. At *E* this would also be the principal factor, although in a boat form non-bonded hindrance due to interaction of the *cis* 1,4 hydrogen atoms may also be involved. The barrier at *C* between the chair and boat forms, or between two chair forms, is also a result of a combination of the same two factors. The barrier (similar to *C* of the figure) between different boat forms of substituted cyclohexanes is probably due primarily to non-bonded hindrance. These examples serve to illustrate the fact that rotational isomerism is not likely to result from *sigma* bond hindrance alone, but commonly arises from a combination of *sigma* bond and non-bonded hindrance.

Thus superimposed on the configurations from the inversional isomerism that occurs when a six-membered ring is suitably substituted, there are eight different conformations possible as a result of restricted rotation about the *sigma* bonds between the atoms which comprise the ring. Of these, two are chair conformations and six are boat conformations. The same situation exists in the case of the pyranose forms of the aldohexoses (XIII), and some of these have been studied rather extensively (*13*).



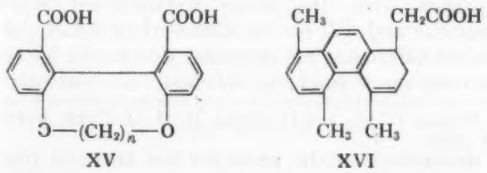
XIII

For the different sugars, depending on the configuration, different conformations are favored as shown by certain reactions such as complex formation, or the formation of anhydro sugars. Methyl 2,6-anhydro-α-D-altropyranoside illustrates how one of the boat forms of the sugar may be locked into position (*14*). This is represented in two different ways (XIV).



XIV

The formulas XV (*15*) and XVI (*16*) are less familiar but more striking examples of structures that may exist in two isolatable conformations as the result of both non-bonded and *sigma* bond hindrance to rotation. In the biphenyl derivative (XV) the two rings are not coplanar; the hindrance to rotation in one direction is due almost entirely to the non-bonded interaction between the two carboxyl groups, while the rotation in the opposite direction is preverted entirely by *sigma* bonds. Although the phenanthrene system (XVI) has been described as a case of stereoisomerism involving bond distortion, it appears that the nonplanar conformation of the rings need involve only rotation about the *sigma* bonds of the atoms which make up the center ring. The general similarity between these cases of rotational isomerism is quite apparent.



XV XVI

Conclusion

The system of classification that has been outlined may be objected to on the grounds that many of the so-called "isomers" are unknown and that their existence cannot be shown by isolation of the compounds. On the other hand, it is often advantageous to make use of concepts which go beyond the present state of actual knowledge and experimentation. In this connection it is of interest that in 1875 van't Hoff (*17*) pointed out that allenes of the type abC=C=Cde should be capable of existence in optically active stereoisomeric forms, and it was 60 years before such compounds were isolated (*18*). This broader and perhaps more fundamental classification to include in better perspective all organic stereoisomers, whether presently isolated or not, would seem to be advantageous.

It should be stated that the proposed classification is concerned with the broad divisions of stereoisomerism and does not imply that symmetry properties and topological relations may not be applied properly and usefully in the designation of the configuration or conformation of individual models. Analogously, we do not base broad chemical classifications of organic compounds on such properties as melting point, density, etc., although we do find these useful in the designation of individual compounds. (The same may be said for the use of the terms "symmetrical" and "unsymmetrical" as applied to disubstituted ethylenes or certain poly-substituted benzene derivatives.) Further, the proposed classification is not an attempt at a specification system for individual models such as that presented by Cahn, Ingold, and Prelog (*19*), nor is it in conflict with that system. The relation to orbital theory may make the proposed system useful by suggesting new approaches to both old and new relationships.

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Isopiestic Vapor Pressure Apparatus

A physical chemistry experiment

The isopiestic method is the most satisfactory technique for the accurate determination of vapor pressures of solutions. Its use as an experiment in elementary physical chemistry would be desirable since the data it affords are of fundamental importance in the physical chemistry of electrolytic solutions.

The usual isopiestic apparatus is not commercially available and is so complex and costly to construct that it would seldom be assembled except for research purposes.

The apparatus proposed by Mason and Gardner[2] for use in physical chemistry experiments requires materials not readily available in many chemistry laboratories. It consisted of a brass desiccator which provided heat conduction between sample cups that were fitted into sleeves soldered to the bottom of the desiccator. A small volume of solution of approximately the same molality as that of the sample solutions was placed in the bottom of the desiccator in order to obtain a more uniform temperature. Stirring of the sample solutions was accomplished by a rocking mechanism and involved movement of the entire apparatus.

More recently Brubaker, Johnson, Knop, and Betts[3] have given detailed directions for the construction of a similar apparatus. However, due to the relative complexity of design, these units might seldom be used in the undergraduate physical chemistry laboratory, particularly at smaller schools where well-equipped machine shops are not available.

Apparatus and Procedure

The experimental requirements for successful isopiestic equilibration are rather stringent and have been thoroughly discussed elsewhere.[4] Our plan for handling these requirements in a simpler way was to float the cups on a swirling solution, thereby accomplishing thermal equilibrium by convection, and stirring of the samples by random motion of the floating cups. The following apparatus and procedure have been evolved to test this plan.

The copper block and brass or steel container were replaced by a solution held in a 150-mm glass vacuum desiccator. The equilibrating solutions were placed in dishes which were then floated on the surface of this reservoir, supported by a float of polystyrene foam. Silver dishes (1-in. bottom diameter; $1^1/_4$-in. top inside diameter with a $^1/_8$-in. lip) obtainable from American Platinum Works, are very satisfactory. They can be seated into holes cut in a disk of polystyrene foam (small enough to turn freely in the desiccator) so that the bottom of the cups sink into the reservoir solution, but the tops are held above the solution. Heat transfer was accomplished by convection aided by a magnetic stirrer operating in the reservoir solution. When a glass constant temperature bath was used, it was found that the magnetic stirrer worked satisfactorily through the bottoms of bath and desiccator. Equilibrium concentrations were preselected by adjusting the reservoir concentration. The glass desiccator tends to damp out bath fluctuations so that any ordinary laboratory thermostat is satisfactory.

The rocking motion of the float as it turned on the swirling reservoir solution gave adequate stirring of the equilibrating solutions in the concentration range studied. More efficient stirring can be obtained by fastening a small bar magnet to the edge of the polystyrene float and another outside the desiccator. By adjusting the position of the outside magnet, one can cause a rocking motion to be induced in the float as the inner magnet passes, thus giving more positive stirring.

The best method of handling the problem of solvent loss, during removal and weighing of cups, was the use of flat lids cut from window glass or lucite. The weighed lids were placed on the cups as soon as the desiccator was opened. There was negligible loss of weight during periods much longer than required to weigh all the samples so that plenty of time could be taken to dry the cups carefully before weighing. This advantage is the most important reason for using smooth cups with rather wide, flat lips.

The procedures used differ only slightly from those employed with the more conventional isopiestic apparatus and will not be discussed in detail. A few obvious differences are necessary due to the floating of the cups on a reservoir solution. In particular the

[1] This work was begun as a senior research project by two of the authors (R. B. H. and J. K.) but was completed by another (G. W. D.) during the summer Research Institute sponsored by the National Science Foundation at Furman University during the summer of 1959.

The authors wish to thank the several students who helped test some of the apparatus and procedures as a part of their regular physical chemistry laboratory assignments. Our thanks are due also to H. S. Kuper and T. C. Patterson for their assistance during the early part of the work and to Victor M. Day for his help in preparing this paper for publication. G. W. D. is indebted to the National Science Foundation for financial support during the summer of 1959.

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evacuation of the system must be done with care. The additional problem with the present approach is bumping of the reservoir solution caused by reducing the pressure too rapidly. The usual method of alternately opening a ballast jar to a vacuum pump and then to the system was employed. Bumping was minimized if the reservoir solution was thoroughly degased prior to beginning a run and kept under vacuum between runs.

Experimental

A total of 26 equilibrations of aqueous solutions using five different solutes were attempted. Of these runs, 17 contributed data for analysis. The remaining nine were discarded for some *known* reason (usually failure of some innovation in apparatus or procedure during the evolution of the recommended method). A few individual samples from the 17 successful runs were discarded for similar reasons. Only three samples were eliminated due to large indeterminate errors.

Periods allowed for the equilibrations ranged from two days to one week, with no significant variation in the quality of the results. The performance is indicated by the weighted average of the deviations per sample from the mean of its replicates which was 0.18% for the 17 successful runs. The table gives the results of five consecutive runs using the recommended procedure.

It is well known that isopiestic experiments are more successful in the concentration range above 1 molal. We have intentionally selected samples in this range because our problem was to prove that vapor pressure equilibrium can be reached in a convection apparatus. The results definitely confirm this. There is every reason to believe that more dilute solutions can be successfully equilibrated in this system but the times required will necessarily be longer than the minimum we have found satisfactory. Actually, once equilibrium has been reached, the more concentrated range provides an equally severe test of the procedures.

Experimental Results (All Values Are Molalities at Equilibrium)

Run No.	Cup 1 NaCl	Cup 2 NaCl	Cup 3 KCl	Cup 4 KCl	Cup 5 KCl	Cup 6 KCl	Av. % dev. from the mean
22	1.174	1.173	1.241	1.231	1.233	1.228	0.22
23	[a]	1.221	1.282	1.284	1.287	1.284	0.11
24[b]	3.021	3.021	3.348	3.343	3.345	3.345	0.03
25	3.010	3.028	3.322	3.325	3.329	3.326	0.15
26	3.018	3.038	3.349	3.345	3.343	3.346	0.16

[a] Sample discarded for a known error.
[b] A minor accident after weighing cup 1 in run 24 caused the small consistent difference between cups 1 and 2 in the last two runs.

The apparatus can easily be assembled and a run started during an average laboratory period. It is convenient to allow the equilibration to proceed until the next period. Completion of the experiment then requires less than an hour.

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Using the Decay of Ba^{137} to Determine Resolving Time in G-M Counting

In the advanced undergraduate chemistry and physics laboratory it has been found desirable to have students not only perform the chemical separation of two radioactive nuclides such as barium and cesium, measuring the half life of the barium daughter, but also to use their measurements to investigate the resolving time, i.e., dead time plus recovery time, of the counting system.

The experiment consists in using an adsorption technique to separate the 2.6-min barium daughter from Cs^{137}, following the decay of the barium over about 10 half lives and making the conventional semilogarithmic plot of counting rate versus time (*1*). For sufficiently large counting rates the curve will not be a straight line but will approach a straight line as resolving time losses become negligible. By extrapolating the straight line portion of the curve, the resolving time loss of the counting system can be read directly from the graph; the resolving time being obtained from the relationship $n - m = nm\tau$ where m is the measured counting rate, n is the rate that would have been obtained with zero resolving time, and τ is the resolving time.

The method used in the separation of Ba^{137} from Cs^{137} is that given by Meites and Thomas (*2*) with slight variation. The separation is dependent upon the selective adsorption of Ba^{137} by $BaCO_3$. The $BaCO_3$ was prepared as follows: 50 ml of a solution containing 0.2 g $(NH_4)_2CO_3$ were added slowly and with stirring to 100 ml of a hot $BaCl_2$ solution (0.6 g $BaCl_2 \cdot 2H_2O$ / 100 ml).

The $BaCO_3$ precipitate was filtered by use of Whatman No. 2,9-cm filter paper and washed four times with hot water. The moist $BaCO_3$ precipitate was scraped onto a spatula and the spatula dipped into a 100 ml Cs*Cl solution (0.006 *M* CsCl to which Cs^{*137} had been added) which was slightly alkaline by addition of a drop or two of dilute ammonia.

The $BaCO_3$ precipitate was allowed to mix with the Cs*Cl solution by stirring for about 25 sec after which the solution was filtered by use of a Büchner funnel using Whatman No. 2,4.25-cm paper. The Ba^*CO_3 precipitate was washed as quickly as possible with 400 ml of water in order to reduce the Cs^{137} background to about 0.5% of the highest counting rate observed. The filter paper containing the Ba^*CO_3 was placed in a standard lead pig containing the Geiger counter, a few millimeters away from the thin (1.4 mg/cm²) mica end window of the counter.

The data for Fig. 1 were obtained using a Baird-Atomic mica end window EWT-64 organic quenched

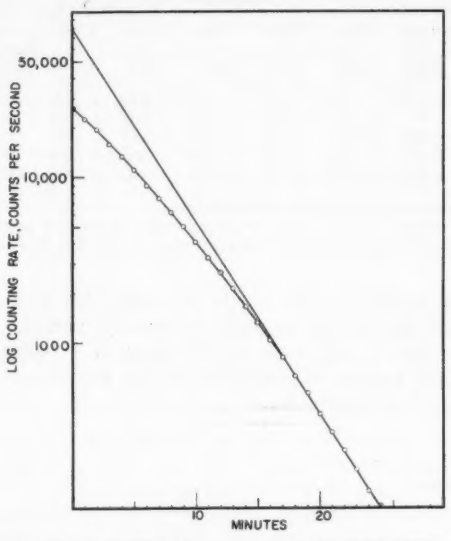

Figure 1. Log of counting rate versus time for Geiger-Müller counting system with small resolving time.

Geiger tube. The counting was done with a Tracerlab SC-51 Autoscaler having a resolving time of 5 microseconds. The counting rate was measured every 30 sec for a 10-sec interval. The source strength of the cesium from which the barium was obtained was approximately 300 microcuries. The cesium can be used indefinitely as a source of the short lived barium and can be purchased from the Oak Ridge National Laboratory with the proper Byproduct Material License.

It is interesting to note the decrease in the effective resolving time as the counting rate increases, varying from about 60 or 70 microseconds to 25 microseconds at t=o. This decrease in resolving time with increasing counting rate and resolving times as low as 10 microseconds for conventional Geiger-Müller tubes have been reported by Muelhause and Friedman (*3*), using fast, sensitive amplifiers. The very fact that some 26,000 counts per sec were observed puts an upper limit on the resolving time of about 39 microseconds at this counting rate since for a non-paralyzable system the measured counting rate must approach $1/\tau$ at high counting rates if τ stays constant. By paralysis it is meant that counts occurring during the resolving time have the effect of extending the resolving time so that with a sufficiently high counting rate the system would register no counts at all. Counting rates as high as 50,000 counts per sec were observed before a decrease in the counting rate was noted, indicating that the system was paralyzable at high counting rates.

Although the resolving time can be determined to within about 10% at the higher counting rates, this is certainly not true as the experimental curve approaches the straight line; at these rates a careful measurement by the two source method (*4*) might be more satisfactory, although the two source method uses the assumption that the resolving time is a constant.

It is important to note that the chemical separation must be good enough so that the cesium background is a negligible fraction of the counting rate at points on the curve where the resolving time is to be measured. It certainly will not be a negligible fraction of the counting rate at times of the order of 10 half lives and must be subtracted to obtain the proper slope for the line.

Figure 2 shows the results of a similar experiment using the same Geiger tube but with a scaler having a resolving time of at least 150 microseconds, clearly showing paralysis at the higher counting rates. The scaler used was the Baird-Atomic 123 glow tube scaler. A cesium source about one tenth the strength of the source for Figure 1 was used. The resolving time of the system is considerably larger than the 150 microseconds supposedly needed to transfer the discharge from one position in the glow tube to the next, being about 300 microseconds at a counting rate of 1380 counts per sec.

Two students, working together, have found it possible to make one such separation and perform all the measurements in one three-hour laboratory period.

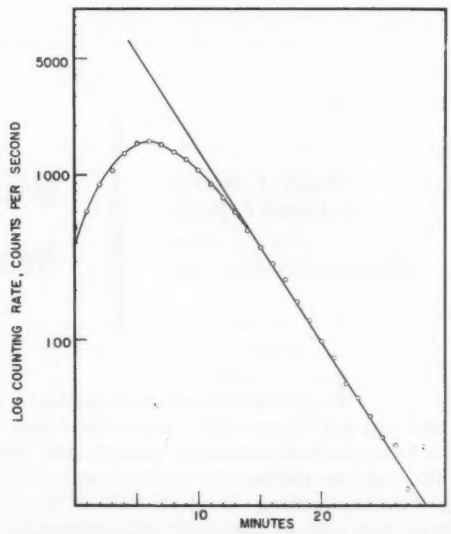

Figure 2. Log of counting rate versus time for a counting system showing paralysis.

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Measurement of the Half Life of $UX_2(Pa^{234})$ with a Dipping Counter

In this paper, a simple measurement of the half life of the short lived isotope $UX_2(Pa^{234})$ is described. This experiment illustrates a number of important principles and useful techniques such as the decay scheme of U^{238}, chemical separation by ion exchange, the measurement of short half lives, and the use of dipping counters. Since the experiment can be carried out in a single laboratory session, it is suitable for a course in radiochemistry or for general chemistry, and it has been used in lecture demonstrations in general chemistry and for the local high school chemistry class. Since the half life of UX_2 is 1.18 min., a measurement of its half life may be completed in about ten minutes. If reasonable results are to be obtained, there must be little time lost between isolation and counting of the samples. In this experiment, the effluent from an ion exchange column is allowed to flow directly into a counting chamber containing a dipping Geiger tube connected to a scaler or ratemeter, and no time is lost in transferring samples.

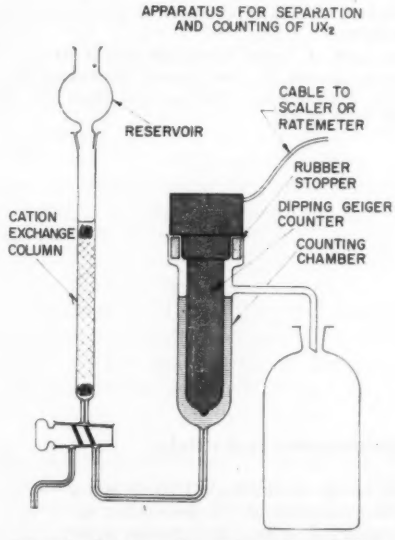

Figure 1. Apparatus for separation and counting of UX_2.

The apparatus is shown in Figure 1. The ion exchange column is made of 11-mm Pyrex tubing, fitted with the female part of a $^{14}/_{35}$ ground joint at the upper end and sealed to a three-way stopcock with 1-mm capillary tubing at the lower end The counting chamber, sealed to the column with 1-mm capillary tubing, is made of 30-mm Pyrex tubing (wide enough to allow about 3 mm clearance between the dipping Geiger tube and the walls of the chamber). The Geiger tube is inserted through a rubber stopper in the neck of the counting chamber and is clamped in place. Solutions are introduced into the column through a 200-ml round bottom flask with the male part of a $^{14}/_{35}$ joint sealed to the bottom. All ground joints and stopcocks are lubricated with a silicone grease. A convenient modification would be the addition of a stopcock at the bottom of the counting chamber to facilitate drainage at the completion of an experiment.

The Experiment

The separation of Pa^{234} follows the procedure of Schweitzer and Whitney (*1*) but avoids the manipulation of samples called for in this and other separations (*2, 3*). A slurry of 80 mesh Amberlite IR-120 (a sulfonated polystyrene) cation exchange resin in water is added to the column after filling the capillary tubes with water and inserting a plug of glass wool in the bottom of the column. The resin is allowed to settle and a column about 15 cm high is formed. A plug of glass wool is placed above the resin and the column is washed with distilled water until the effluent is clear. One hundred ml of a solution containing 10 g uranyl nitrate is allowed to flow through the column at a rate of two to three drops per sec. The uranyl nitrate solution is recovered for reuse after the equilibrium UX_1 content has been reattained. The column is washed successively with 100 ml of water, 200 ml of 0.3 *N* H_2SO_4, and 100 ml of H_2O, at a rate of about five drops per sec (stopcock completely open with the system described). (The effluent should be colorless, indicating removal of uranyl ion.) Uranyl ion is eluted from the column by the sulfuric acid solution leaving the more strongly held daughter UX_1 (Th^{234}) on the column. The reservoir is filled with 5% HCl which is allowed to flow through the column and into the counting chamber with the stopcock completely open and the counter in operation. When the ratemeter indicates a plateau in the counting rate, the stopcock is closed and the counting rate is read at 10 or 15 sec intervals until the counting rate has dropped to the background level (5 to 10 min). Pa^{234} is eluted from the column by the HCl leaving its parent Th^{234} behind. Experimental results are shown in Figure 2 as a plot of the activity of Pa^{234} as counts/min (corrected for background) versus time. The half life is found to be 1.21 ± 0.03 min, compared to the accepted value of 1.18 min (*4*). The counting was done with a dipping Geiger tube having a glass wall of thickness 30 mg/cm² (Tracerlab TGC-5) connected to a Tracerlab SU-3D Laboratory Monitor, using the 11 sec time constant circuit.

Measurements also were made with the dipping counter connected to a Baird-Atomic #123 scaler. The total number of counts was recorded at 10-sec. intervals and the data, corrected for the background

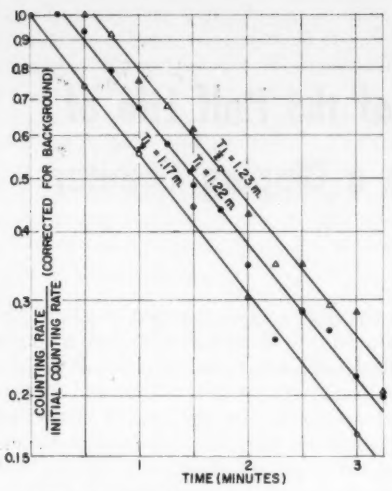

Figure 2. Half life of UX_2 (Pa^{234}).

count, are shown in Figure 3. The half life was calculated from the relation

$$T_{1/2} = \frac{0.693\ T}{\ln\ [c_\infty/(c_\infty - c)]}$$

where c_∞ is the total number of counts at infinite time and c is the total number of counts accumulated at the time T. The average value of $T_{1/2}$ calculated from 21 data points (excluding three points for which the deviation from the average exceeded twice the standard deviation) was 1.21 ± 0.03 min.

Since the half life of UX_1 (Th^{234}) is 24.1 days, the prepared column may be used as a source of UX_2 for about a month. It can be used in lecture demonstrations by eluting Pa^{234} into the counting chamber with the HCl solution. The half life of UX_1 may be determined by

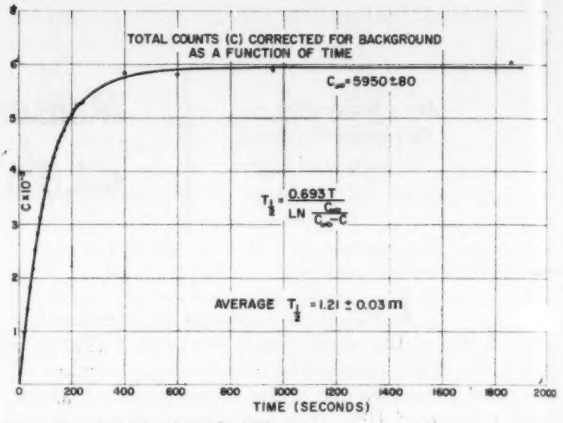
TOTAL COUNTS (C) CORRECTED FOR BACKGROUND AS A FUNCTION OF TIME
C∞ = 5950 ± 80
T½ = 0.693 T / LN C∞/(C∞−C)
AVERAGE T½ = 1.21 ± 0.03 m
C × 10⁻³
TIME (SECONDS)

Figure 3. Half life of UX_2 (Pa^{234}).

observing the plateau counting rate obtained on elution with HCl at weekly intervals. Additional experiments involving the elution of UX_1 from the column (e.g., with oxalic acid) also may be performed.

Acknowledgment

The Radiochemistry Laboratory at the University of Maine was made possible by a grant from the Atomic Energy Commission. We gratefully acknowledge the assistance of E. Thomas, G. Dunn, and D. Foley.

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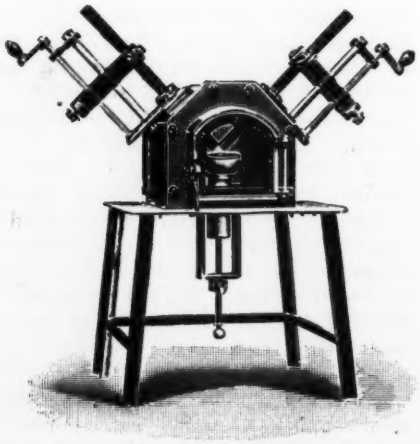

Smithsonian Seeks Help

The Smithsonian Institution's United States National Museum presently is developing exhibits of chemistry for a new museum now under construction.

They are seeking an example of the Moissan electric furnace, here pictured. This has not been accomplished yet, and the Museum asks the assistance of readers of this journal in locating an example of this furnace for their collection.

Any information should be sent to Mr. Robert P. Multhauf, Head Curator, Department of Science and Technology, Smithsonian Institution, Washington 25, D. C.

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A New Derivation of the Boltzman Distribution Law

The derivation to be presented is identical in most respects with the usual one. It differs from the latter mainly in that the Stirling approximation is not employed; an approximation is necessary, but the particular approximation which is used here has the merit that it can be introduced at the very end of the derivation. The discussion of "thermodynamic" probability is also somewhat different; it is based on "ordinary" concepts of probability, which are at least somewhat familiar to students; and further clarity is achieved, it is felt, by bringing in Heisenberg's uncertainty principle, by which is made apparent the need for the concept of "phase space," in terms of which the thermodynamic probability can be rigorously defined.

Let us consider a macrosystem which consists of numerous particles such as molecules. These particles need not be independent of one another; that is, they may have mutual potential energy. Since the system is made up of a large number of parts, there are a great many different ways of arranging its parts to give the same thermodynamic state, although at any one instant the system has just one of these arrangements. The probability that the system exists in a given thermodynamic state is then equal to the probability that it exists in *any* one of the many possible arrangements that correspond to this particular thermodynamic state. Because only one arrangement can occur at a time, the probability that the system exists in *any* of the arrangements equals the sum of the probabilities of each separate arrangement. By considerations of symmetry, each separate arrangement is equally probable. Thus the sum of the probabilities of each separate arrangement is equal to the total number of separate arrangements, which is called the "thermodynamic probability" of the system, times the probability of each separate arrangement. That is,

$$p_N = W_N p_1$$

where p_N = the probability of the system, W_N = the total number of different possible arrangements of the N particles which comprise the system, and p_1 = the probability of each separate arrangement.

We are now faced with the question as to what is actually meant by the "separate arrangements" of the system. To avoid any ambiguity, we should rely on definitions which are related to what we are able, at least in principle, to observe. Heisenberg showed that it is not possible to observe simultaneously both the position and the momentum of an object with complete precision. Accordingly, it is customary to (1) consider an abstract six-dimensional space, called the "phase space" of the particles, of which the coordinates are the three ordinary position coordinates and three additional coordinates corresponding to the components of momentum, (2) divide this space into "cells" of equal volume, and (3) note which cell a given particle is in. This "observation" specifies the position and the momentum of the particle within the limits of the location and dimensions of its cell in phase space, in complete harmony with Heisenberg's uncertainty principle.

On this basis, we can define the total possible number of separate ways, W_N, in which the system of N particles can be arranged, to give the same thermodynamic state, as the total number of *distinguishable* permutations of the N particles among the cells of phase space. (This is a reasonable definition because a permutation must be distinguishable to be observable.)

(Alternatively, we may consider the phase space of the macrosystem. This is a $6N$-dimensional abstract space, the coordinates of which are the position and momentum coordinates of each of the N particles of the macrosystem. Then W_N is equal to the number of cells occupied in the phase space of the macrosystem. In this $6N$-dimensional phase space, each point is called a "representative point" because it represents the entire macrosystem.)

If each particle of the macrosystem is different, as by possessing a different amount of energy, then each permutation of the particles is distinguishable; for a system of N particles, the total number of distinguishable permutations would then be $N!$ If the particles differ only in having different amounts of energy, but N_1 particles have energy e_1, N_2 particles have energy e_2, etc., then the total number of distinguishable permutations will be less than $N!$ because permutations of particles having identical energy are not distinguishable; in this case, the total number of distinguishable permutations is given by $N!/N_1! \times N_2! \times \ldots$. Therefore the probability of the system is

$$p_N = (N!/\Pi N_i!)p_1$$

It is necessary to distinguish between the thermodynamic state and the "statistical state" of a system. In classical thermodynamics, the state of a system is defined only at equilibrium. If the system is not at equilibrium, its state can be defined statistically by enumerating the particles having various energies. (The number of particles N_i having the same energy e_i is called the "population," "occupation number," or "occupancy" of energy level e_i.)

According to the second law of thermodynamics, a system which is not at equilibrium will tend toward its equilibrium state, that is, its thermodynamic state. Thus the thermodynamic state of a system is the same as its most probable statistical state.

Another way of phrasing this conclusion is that the probability of the thermodynamic state is equal to the maximum probability of the statistical state, meaning p_N is at a maximum for the thermodynamic state. Equivalently, since p_1 is a constant, the number of distinguishable permutations, W_N, is at a maximum. The condition for the thermodynamic state—that is, for equilibrium—is then given by either

$$\delta p_N = 0 \qquad \text{or} \qquad \delta W_N = 0$$

Hence

$$\delta(N!/\Pi N_i!)p_1 = \delta(N!/\Pi N_i!) = 0$$

for equilibrium. For mathematical convenience, we shall use the logarithm instead. We then have the equilibrium condition

$$\delta \ln (N!/\Pi N_i!) = \delta \ln N! - \Sigma\, \delta \ln N_i! = 0$$

Since N (the total number of particles in the system) is a constant, $\delta \ln N! = 0$, whence the condition for equilibrium becomes simply

$$\Sigma\, \delta \ln N_i! = 0$$

The fact that $N = \Sigma N_i$ is a constant introduces the further condition

$$\delta N = \Sigma \delta N_i = 0$$

Since the statistical state of a system is defined in terms of the number of particles N_i having a given energy e_i, enumerated over the various values of the energy possessed by the particles of the system, the energy is also a variable that we should investigate. The energy of the system, being the sum of the energies of the particles which comprise the system, depends on the occupation numbers N_i of the energy levels e_i as follows:

$$E = \Sigma\, N_i e_i$$

The thermodynamic properties of a system, being statistical averages, are unaffected by the occurrence of any permutations of the particles of the system, as long as all of these permutations correspond to the same thermodynamic state. Hence the energy of the system, which is a thermodynamic property of the system, is a constant when the system is at equilibrium. This introduces a third condition for equilibrium:

$$\delta E = \Sigma\, \delta\, N_i e_i = \Sigma\, e_i\, \delta N_i = 0$$

(In words, the energy of a system at equilibrium is not affected by fluctuations in the occupation numbers of the energy levels of the system. This is merely another way of saying that the permutations of the particles do not affect the energy of the system, which is a statistical average.)

We have found three conditions for equilibrium. What single condition for equilibrium do they represent? To find this single condition, it is clearly necessary to combine the three separate conditions. Two of them involve the fluctuation δN_i while the remaining one involves $\delta \ln N_i!$ instead, whence the three conditions do not all have a common basis. To combine all three, it is necessary to express $\Sigma\, \delta \ln N_i!$ in terms of δN_i.

By calculus we have[1]

$$\begin{aligned} d \ln x! &= d \ln [1 \cdot 2 \cdot 3 \ldots (x-2)(x-1)x] \\ &= \sum_{m=0}^{x-1} [d \ln (x-m)] \\ &= \sum_{m=0}^{x-1} [1/(x-m)]\, d(x-m) \\ &= \sum_{m=0}^{x-1} [1/(x-m)]\, dx \\ &= (1 + {}^1/_2 + {}^1/_3 + \ldots + 1/x)\, dx \end{aligned}$$

whence

$$\Sigma\, d \ln N_i! = \Sigma(1 + {}^1/_2 + {}^1/_3 + \ldots + 1/N_j + \ldots + 1/N_i)\, \delta N_i = 0$$

We can combine the three conditions $\Sigma\, \delta N_i = 0$, $\Sigma\, e_i\, \delta N_i = 0$, and $\Sigma(\Sigma\, 1/N_j)\, \delta N_i = 0$ by Lagrange's method of undetermined multipliers. In this method, all but one of the conditions are multiplied by unknown parameters, a, b, ..., and then the various conditions are added together. Thus we have

$$a\, \Sigma\, \delta N_i + b\, \Sigma\, e_i\, \delta N_i + \Sigma(\Sigma\, 1/N_j)\, \delta N_i = 0$$

or

$$\Sigma(a + be_i + \Sigma\, 1/N_j)\, \delta N_i = 0$$

This is the single condition for equilibrium.

Since the fluctuations in the various occupancies, δN_i, $i = 0, 1, 2, \ldots$, are presumably independent, it follows that

$$(a + be_i + \Sigma\, 1/N_j)\, \delta N_i = 0$$

for each i, that is, for each separate energy level. Granting that fluctuations do occur, $\delta N_i \neq 0$, we then find that

$$a + be_i + \Sigma\, 1/N_j = 0$$

This is an exact result, provided that the assumption of the independence of the fluctuations is correct; the form of this result also depends upon our definition of the thermodynamic probability, W_N. We shall now use this result to find N_i explicitly in terms of e_i.

Unfortunately, as there is no known simple expression for the sum of a harmonic series, it is not possible to solve this equation explicitly for N_i. It is therefore necessary to find an approximate sum for $\Sigma\, 1/N_j$ in terms of N_i which can be solved explicitly for N_i.

The terms in the infinite series[2]

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[1] The formula $d \ln x! = (1 + {}^1/_2 + {}^1/_3 + \ldots + 1/x)\, dx$ is not listed in any books that the author has seen even though it is a very simple and aesthetically appealing result.

[2] This series expansion of $\ln N_i$ can be derived in a simple manner. By ordinary long division of $(1 - x)$ into 1, we find that

$$1/(1-x) = 1 + x + x^2 + x^3 + \ldots$$

where the series is infinite. The same result is obtained by Newton's binomial expansion of $(1 - x)^{-1}$. Then

$$\begin{aligned} \int_0^u (1 + x + x^2 + x^3 + \ldots)\, dx &= \int_0^u [1/(1-x)]\, dx \\ &= -\int_0^u [1/(1-x)]\, d(1-x) \\ &= -\ln (1-u) \end{aligned}$$

Integration of the lefthand side, term by term, gives the familiar expansion

$$-\ln (1-u) = u + u^2/2 + u^3/3 + \ldots$$

Letting $u = (N_i - 1)/N_i$ in this expansion then gives the desired result.

$$\ln N_i = (N_i - 1)/N_i + [(N_i - 1)/N_i]^2/2 + [(N_i - 1)/N_i]^3/3 + \ldots$$

approach the corresponding terms in the harmonic series

$$\Sigma\, 1/N_i = 1 + 1/2 + 1/3 + \ldots + 1/N_i + \ldots + 1/N_i$$

as $(N_i - 1)/N_i$ approaches unity, that is, as N_i approaches infinity.

The number of terms in the harmonic series approaches infinity as N_i approaches infinity. Thus the two series approach one another as N_i approaches infinity. For very large values of N_i, therefore, we have the convenient approximation, which does not appear to have been given previously,

$$1 + 1/2 + 1/3 + \ldots + 1/N_i \approx \ln N_i$$

from which

$$a + be_i + \ln N_i \approx 0$$

or

$$N_i \approx A \exp(-be_i)$$

This approximate result is one form of the Boltzmann distribution law. It gives the number of particles, N_i, having the energy e_i. The coefficient $A = \exp(-a)$ is called the "absolute activity" of the macrosystem.

The other form of the Boltzmann distribution law gives the fraction of particles, N_i/N, having the same energy e_i:

$$\begin{aligned} N_i/N &\approx A \exp(-be_i)/N \\ &\approx A \exp(-be_i)/\Sigma N_i \\ &\approx A \exp(-be_i)/\Sigma A \exp(-be_i) \\ &\approx \exp(-be_i)/\Sigma \exp(-be_i) \end{aligned}$$

or

$$N_i/N \approx \exp(-be_i)/Q$$

where Q is called the "partition function" of the particles. (We see that the absolute activity and the partition function are related by $A = N/Q$.)

If the same value of the energy, e_i, can be achieved in g_i different ways, then the energy level e_i is called "degenerate." (A more civilized and more descriptive name would be "multiple.") And g_i is called the "degeneracy," "multiplicity," or "statistical weight" of energy level e_i. When this is the case, the Boltzmann distribution law must be modified. The occupancy of energy level e_i corresponding to *each one* of the various ways of obtaining the same value of the energy e_i is then

$$N_i/g_i \approx A \exp(-be_i)$$

hence the two forms of the Boltzmann distribution law are

$$N_i \approx A\, g_i \exp(-be_i)$$

and

$$N_i/N \approx g_i \exp(-be_i)/Q$$

where $Q = \Sigma\, g_i \exp(-be_i)$. These are the most general ways of writing the Boltzmann distribution law. (We still have $A = N/Q$.)

It remains only to show that $b = 1/kT$, where k is Boltzmann's constant (the ideal gas constant R divided by Avogadro's number) and T is the absolute temperature. It seems that the only way to do this at the present time is by the usual method: derive equations with the aid of the distribution law and compare the results with those of classical thermodynamics. Some authors prefer to define the absolute temperature by $T = 1/kb$. The present author would rather rely on classical thermodynamics because the Boltzmann distribution law is only an approximation, albeit a mathematically convenient one. (In particular, it holds poorly at low temperatures.)

NSF Summer Institutes in Chemistry

The National Science Foundation has announced grants to support 30 summer institutes designed especially for teachers of chemistry, to be held during the summer of 1961. Of these, 23 are directed toward high school teachers, four are for high school and college teachers, and three are designed primarily for college teachers.

Part of a group of 395 summer institutes receiving NSF support for summer 1961, the institutes for chemistry teachers will be held at colleges and universities in 21 states. At least 130 additional institutes will include chemistry courses in their programs. Details on each of the summer institutes for chemistry teachers follow. More information is available from the institute director.

For College Teachers

Emory Univ., Jun 12-Aug 11: Modern developments in chemistry, with emphasis on the theory of chemical bonding and the evidence for molecular structure, with their implications for the properties of matter. W. H. Jones (Chem.).

Univ. of North Carolina, Jun 12–July 21: Modern developments in the major branches of chemistry; experimentation in modern laboratory techniques; seminars. H. D. Crockford (Chem).

Oregon State College, Jun 26-Aug 5: Recent developments in analytical, inorganic, and organic chemistry; principles of physical chemistry. A. V. Logan (Chem).

For High School and College Teachers

Harvey Mudd College, Jul 15–Aug 26: Intensive investigation of Chemical Education Material Study text, laboratory experiments, films, etc.; for teachers who during the 1961–62 school year will be utilizing CHEM Study materials. L. E. Malm (CHEM Study).

Montana State College, Jul 16–Aug 17: Recent advances and significant trends in physical, analytical, organic, inorganic, and biochemistry; high school refresher; elementary radiochemistry. L. O. Binder, Jr. (Chem).

Philadelphia College of Pharmacy and Science, Jul 10-Aug 18: Radiochemistry, for teachers of biology, chemistry, and physics. Arthur Osol (School of Chemistry).

Tufts Univ., Jul 5-Aug 18: The Chemical Bond Approach course in high school chemistry. M. K. Wilson (Chem).

For High School Teachers

Bowdoin College, Jun 26–Aug 5: Fundamental concepts of chemistry, for teachers who teach or are preparing to offer an advanced placement chemistry course. S. E. Kamerling (Chem).

Brown Univ., Jun 26-Aug 5: The Chemical Bond Approach to high school chemistry. L. B. Clapp (Chem).

Central College, Jun 5-Aug 4: Fundamentals of the science of chemistry. N. C. Nielsen (Chem). (*Continued on page 38*)

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Student Experiment with Filter Paper Electrophoresis

The effect of electrical charge in determining some of the properties of amino acids and proteins can be simply and convincingly demonstrated to the student by means of filter paper electrophoresis. The construction and application of a simple filter paper electrophoresis apparatus is described below.

A systematic diagram of the inexpensive direct current source is shown in Figure 1. Its appearance as connected to the electrophoresis assembly is shown in Figure 2. The components were as follows:[2]

1 miniature type selenium rectifier, such as Sarkes Tarzian, Model 50.
1 Neon Glow Lamp, 2-watt, Edison base, such as G.E. NE-34.
1 1/16-amp A.G.C., rapid action fuse, such as the Buss (250-v maximum) fuse; fuse holder, connecting wire, power cord, alligator clamps and graphite squares.[3]

The total cost for each unit was approximately $2.80. Working in a production line two persons can assemble about eight units per hour. When no load is imposed, the output of the power supply is about 30 v. The oversized neon lamp is simply a warning to indicate when the apparatus is plugged in. The rapid-action fuse provides additional protection.

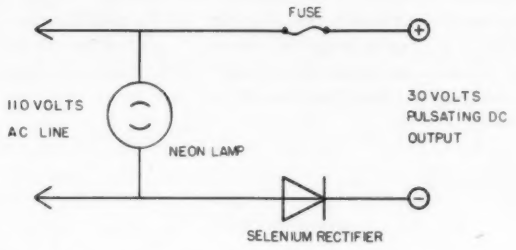

Figure 1. Schematic diagram of pulsating dc power supply

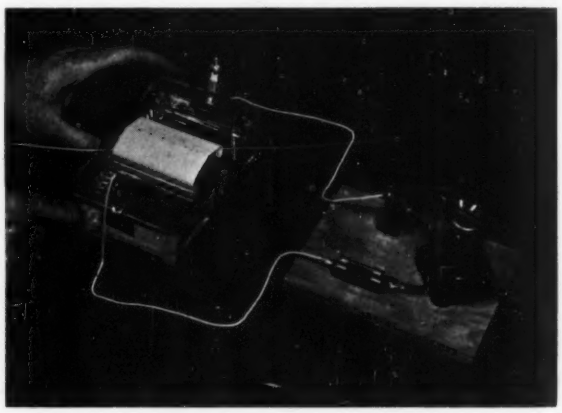

Figure 2. Photograph of student filter paper electrophoresis apparatus.

The Experiment

The appearance of the apparatus just before covering it and starting a run is shown in Figure 2. The procedure is as follows:

A piece of Whatman No. 1 filter paper is cut to exactly 7 × 12 cm. Seven channels running the long axis of the paper are drawn with a lead pencil and ruler, and then three lines are drawn at right angles across these channel boundaries—one across the exact middle (the point of application of the materials to be analyzed) and two additional lines parallel to the starting line and 2.5 cm to each side. The paper is next made to look like a little house by folding along the center line and then in the same direction along the two other lines (Fig. 2).

Still keeping the paper dry, the amino acids, protein and protein hydrolysate are applied with wooden applicator sticks. A tiny drop of each solution is applied to the center of the channel opposite the appropriate label. The moist dots should be no more than 2 mm in diameter. The spots are then allowed 5 min. to dry.

The apparatus is now assembled as seen in Figure 2. The two reservoir dishes (histological staining dishes) are placed with their long edges parallel and about 5 mm apart on a rectangle of Saran Wrap about 30 × 45 cm in size. The dishes should be arranged so that the apparatus can be enclosed by the film when it is set up. The apparatus must be covered during operation or evaporation may distort the electrophoretic patterns. A microscopic slide is inserted into the next to last slot on each of the adjoining sides. Then the two carbon electrodes are clamped to the far edges of the two dishes with the alligator clamps. The clamps must be kept high enough so that they are above the liquid level or there will be active electrolysis.

The paper house is now lowered into the dishes so that it rests as shown in Figure 2. The sides of the little house fit down between the microscopic slides and the walls of the reservoir vessel. The reservoir dishes are filled simultaneously with 100 ml each of 0.01*M* phosphate buffer of *p*H 7.0. If it looks as though the advancing liquid fronts will not reach the

[1] United States Public Health Service Senior Research Fellow No. 238. This contribution was supported in part by RG-4734 from the National Institutes of Health and the Edris Fund.

[2] All components except the graphite squares were purchased from Allied Radio, 100 N. Western Avenue, Chicago 80, Illinois.

[3] Discarded centrifuge brushes can be used. The graphite must be thin enough to allow the alligator clamp to hold both the side of the reservoir vessel and the graphite electrode.

loaded zone simultaneously the laggard is encouraged with a little buffer on a clean applicator stick. The entire assembly is covered with the Saran Wrap. The upper ends of the alligator clamps may be used for support. The power supply is plugged into a 110-ac source and allowed to run for about 50 min.

When the time is up the apparatus is disconnected and the paper carefully lifted out and allowed to dry for about 20 min. A ninhydrin reagent (0.2% ninhydrin in 1/1, alcohol/acetone is satisfactory) can now be either sprayed or squirted on and another 10-min. drying period allowed. Heating for a few minutes at 90°C will bring out the spots.

A result obtained in 50 min. by the author is shown in Figure 3. Student results were not uniformly this elegant but almost without exception were qualitatively interpretable in the same manner. The positively charged lysine has moved toward the negative pole, the negatively charged glutaminic acid has moved toward the positive pole, and the neutral valine has remained close to the point of application. The mixture of lysine, valine, and glutamic acid is well separated. The splitting of the albumin hydrolysate into three fractions can be seen, while the unhydrolyzed albumin moved but little.

Although other amino acid combinations can be used, we selected glutamic acid, valine, and lysine because they have been shown to govern the electrophoretic migrations, respectively, of hemoglobins A, S, and C.[4,5] Electrophoretograms of hemoglobins obtained from a clinical laboratory (from normal individuals and from patients with sickle cell disease, sickle cell train, and hemoglobin C disease) were demonstrated during the laboratory period. By

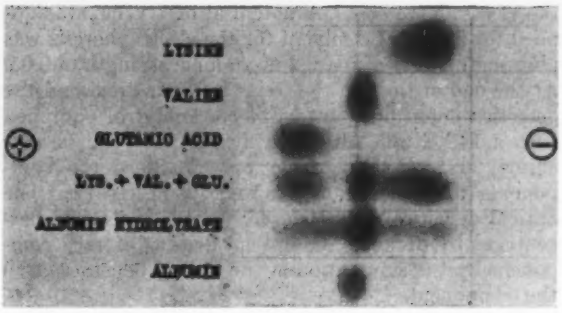

Figure 3. Photograph of electrophoretogram made with student apparatus.

comparison with his own results, the student was able to see that the electrophoretic properties of these different hemoglobins are indeed explained by the dissociation properties of the three amino acids. As a further exercise, each student was required to furnish structural formulas and ionic species of glutamic acid, valine, and lysine as they exist in the free state at *p*H 7.0 and as they occur in the polypeptide side chain of the several hemoglobins at *p*H 8.6.[6]

[4] Ingram, V. M., *Nature*, **180**, 326 (1957).
[5] Hunt, J. A., and Ingram, V. M., *Nature*, **181**, 1062 (1958).
[6] The amino acid solutions were all 0.01*M* in 0.01*M* phosphate buffer of *p*H 7.0. It is necessary to bring the glutamic acid solution to *p*H 7.0 with 0.1*N* NaOH. The ovalbumin hydrolysate was prepared by heating a 2.5% ovalbumin solution with 6*N* HCl for one hour. Overnight, of course, would give more complete hydrolysis. The hydrolysate was evaporated to dryness under vacuum several times to remove the HCl, taken up in 0.01*M* phosphate buffer, and brought to *p*H 7.0 with sodium hydroxide.

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Paper Electrophoretic Study of Rates of Consecutive Reactions: the Deamidation of Vitamin B_{12}

The deamidation of vitamin B_{12} to form carboxylic acids was first reported by Armitage, *et al.*,[1] in connection with the determination of the vitamin's structure. Our interest in this reaction stemmed from a report by Smith[2] on the instability of radioactive B_{12} and from our own findings[3] that the degradation products were the corresponding carboxylic acids. Paper electrophoresis was used to evaluate the kinetics of the reaction of unlabeled vitamin B_{12}, particularly to see if there was evidence for autocatalysis.

Crystalline vitamin B_{12} was dissolved in 0.2*N* HCl to a concentration of 1% and kept at room temperature in the dark. At intervals of one or two days samples were removed and examined electrophoretically. Twenty μl of the test solution was applied to the center of a strip of Whatman 3-mm paper suspended between

[1] Armitage, J. B., et al., *J. Chem. Soc.*, 3849 (1953).
[2] Smith, E. L., *The Lancet*, **1**, 387 (1959).
[3] Barlow, G. H., and Sanderson, N. D., *Biochem et Biophys. Acta.*, **41**, 146 (1960).

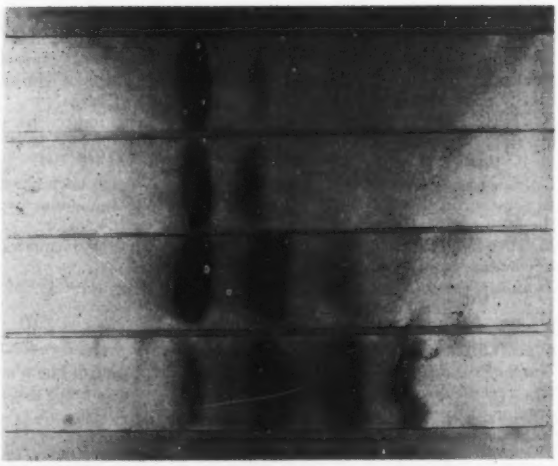

Figure 1. Paper strips on deamidation process. From top to bottom: one day; two days; three and half days; fourteen and half days.

the electrode vessels. A potential of 7 v/cm was applied for 5 hr. The solvent for the electrophoresis was phosphate buffer of pH 6.2 at an ionic strength of 0.05. At the end of the run the strips were air dried and the densities determined in a Spinco Analytrol equipped with a B-2 cam. Alternatively the strip can be cut, eluted, and read in a colorimeter. Since the components are colored no staining is necessary. The optical densities were then converted to relative percentages by dividing the optical density of each component by the summation of the optical densities of all the components.

Figure 1 shows a typical series of the strips obtained at various times from a sample of a solution containing vitamin B_{12}. The original material which shows only one peak at $t = 0$ develops with time a second, a third, and ultimately a fourth peak. Vitamin B_{12} itself moves toward the cathode, while the carboxylic acids formed by the deamidation process move toward the anode.

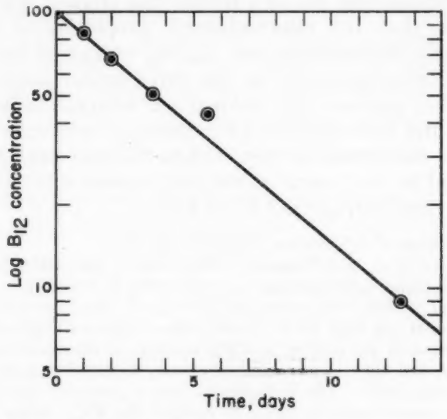

Figure 2. Plot of log B_{12} remaining versus time.

Figure 2 is a plot of the log of residual vitamin B_{12} versus time. It is clear the reaction is first order. The constant calculated from the slope is 0.83 $days^{-1}$. These data rule out the possibility of autocatalysis, since such an excellent linear relationship would not be obtained if autocatalysis were involved.

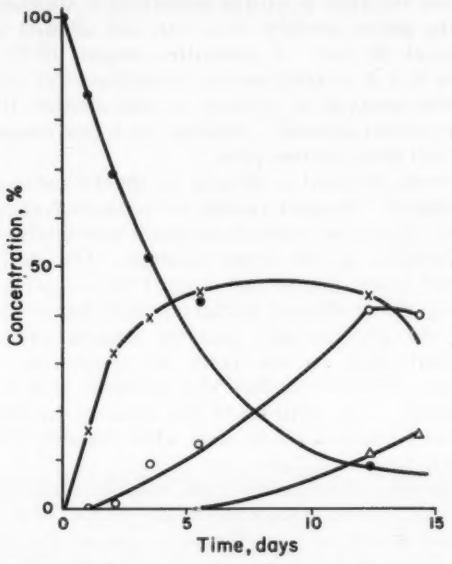

Figure 3. Plot of data on per cent of all the components ● vitamin B_{12}; X monocarboxylic acid; ○ dicarboxylic acid; △ tricarboxylic acid.

Figure 3 is a complete diagram of the percentage of each of the components present at various times. It provides a very graphic illustration of the variation of concentration with time for each of the intermediates in a series of consecutive first order reactions of the type A→B→C→D. Except perhaps in radioactive decay chains, there are few systems in which all the intermediates can be seen directly.

NSF Summer Institutes—Continued from p. 35

Colorado State College, Jun 24–Aug 18: Structure of matter; organic chemistry; analytical chemistry. John A. Reel (Chem).

Colorado State Univ., Jun 19-Aug 11: Chemistry; for teachers of advanced placement courses. G. H. Splittgerber (Chem).

Cornell University, Jul 17-Aug 26: Intensive investigation of Chemical Education Materials Study text, laboratory experiments, films, etc.; for chemistry teachers who will use CHEM Study materials during 1961–62. M. L. Nichols (Chem).

Earlham College, Jun 26-Aug 4: CBA chemistry; for teachers interested in the Chemical Bond Approach course development. L. E. Strong (Chem).

Univ. of Illinois, Jun 19–Aug 12: Principles of chemistry (special problems in the teaching of high school chemistry); the status of modern chemistry. A. M. Hartley (Chem).

Indiana Univ., Jun 14–Aug 11: Principles of chemistry; courses in chemistry. R. B. Fischer (Chem).

Juniata College, Jul 10-Aug 20: Chemical equilibrium. D. M. Hercules (Chem)

Kenyon College, Jun 25-Aug 5: The properties of the chemical bond (CBA chemistry). E. S. Graham (Chem).

Univ. of New Hampshire, Jun 26–Aug 18: Principles of chemistry, recent developments and trends in chemistry, analytical, organic, physical, and radio; research participation. H. A. Iddles (Chem).

The Agriculture and Technical College of North Carolina, Jun 12–Aug 11: Modern analytical chemistry, elements of organic chemistry; mathematics for chemists. G. A. Edwards (Chem).

Univ. of Notre Dame, Jun 19–Aug 3: Principles of chemistry. E. T. Hofman (Chem).

College of the Pacific, Jun 19–Aug 25: Chemistry and mathematics. Alexander Vavoulis (Chem).

Purdue Univ., Jun 18–Aug 11: Chemistry. D. A. Davenport.

Reed College, Jun 18–Jul 29: The Chemical Bond Approach course in high school chemistry. A. H. Livermore (Chem).

Univ. of Rochester, Jun 26–Aug 4: Modern concepts of general chemistry (Director, R. M. Whittaker, Queens College.) Write J. J. Montean (College of Education).

College of St. Thomas, Jun 19–Jul 29: Modern chemistry for high school teachers. Martin Allen (Chem).

Southwestern State College, Okla., June 5–Jul 27. The structure of matter; the chemistry of solutions; the chemistry of reaction types; teaching chemistry in the high school. E. A. Reynolds (Math and Phys. Sci.).

Tuskegee Institute, Jun 5–July 29: Modern concepts of chemistry; essential principles of organic chemistry and life processes; physical chemistry; fundamental concepts in mathematics; methods of teaching chemistry. L. F. Koons (Chem).

Univ. of Washington, Jul 17–Aug 18: Fundamental presincipl of chemistry; experimental methods in chemistry. E. C. Lingafelter (Chem).

Wisconsin State College at Superior, Jun 12–Aug 5: Modern concepts in inorganic and analytical chemistry; modern concepts in organic and physical chemistry. J. W. Horton (Chem).

A Pioneer Summer Institute

The General Electric Science Fellowship Program at Union College

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The summer institute for high school science teachers was pioneered in 1945 at Union College as a college-industry venture. It was known as the General Electric Science Fellowship Program. After 15 years of successful operation, the program was terminated in the summer of 1959. The reason for the termination of the program was due largely to a decrease in the number of applicants as a result of the large increase in the number of summer institutes, particularly those sponsored by the National Science Foundation. There was also a desire on the part of the General Electric Company to develop their educational activities in other areas.

The program has served as a model for other industry-sponsored programs as well as the National Science Foundation Summer Institutes. Like these similar programs, its aim was to advance teaching techniques and knowledge in the fields of basic science by bringing teachers up to date in their respective fields. Originally the program was limited to the fields of chemistry and physics and served the Eastern area of the country and the Atlantic seaboard as far south as North Carolina. Later, similar company-sponsored programs were added in other geographical areas, and one was added especially for mathematics teachers. The total number of Fellows who participated in all the programs was of the order of 2500.

This report is concerned only with the program at Union College and, in particular, with the chemistry part.

There was a yearly quota of approximately 50 Fellows, half of whom were in chemistry and half in physics. The College assumed the responsibility for the selection of the Fellows, the general administration, and all planning and implementation of the academic operation. The staff consisted of a director, two instructors in chemistry, and two in physics. Selected personnel of the company assisted in the planning and the execution of certain phases of the program.

During the 15 years, some concepts of the program as well as many details were subject to change and modification. The original concept of a course content at a truly graduate level was modified to the reality of the science backgrounds of the participating Fellows. While the maturity of approach was retained, much of the course work was selected from that which would be encountered in the undergraduate college chemistry curriculum.

During the six-weeks' program, the course work consisted each week of five lectures at 8 A.M., attended by all the Fellows; three 9 A.M. lectures in chemistry only for the chemistry Fellows and similar lectures in physics for the physics Fellows; two laboratory periods of three hours each for the chemistry group and the same for the physics group. Two afternoons each week were devoted to inspection trips to the numerous area plant and laboratory facilities of the General Electric Company. In addition, there were a number of lectures by particularly distinguished scientists of the company.

Lecture Program

Most of the 8 A.M. lectures were given by selected scientists from the General Electric Research Laboratory. Each was on a different subject. They covered such diverse topics as: Bohr theory, coordination compounds, polymers, rocket propellants, semiconductors, reactors, rheology, microwaves, geochemistry, and astrophysics. Each year the topics varied somewhat, depending on the availability of effective speakers in the desired areas. The Fellows appreciated the printed outlines that were distributed before each lecture. These were of particular value for those talks given at a rather high level. Each Fellow was required to keep a well developed set of notes which were inspected and graded by the teaching staff.

The nine A.M. lectures were coordinated with the laboratory. For the Chemistry Fellows, the title for the course was "Modern Chemistry in Theory and Experiment." From year to year the subject matter of the lectures and the experiments performed varied somewhat. For the limited time available (18 lectures and 10 laboratory periods), it was difficult to select material that would present a coherent and meaningful course. In the latter years of the program, the concept of the course was developed around the idea that chemistry was an experimental science based on the laboratory. The function of the laboratory was given as threefold: first, to make measurements; second, to analyze; third, to prepare something. Thus, the facts obtained from the laboratory served as a background for the theories, principles, and descriptive material that was presented in the lecture. This included such topics as: the mathematical treatment of data, the plotting of curves, electrolytes, equilibria, chemical kinetics, electrode potentials, light absorption in chemical systems, and theories of atomic structure and chemical bonding.

Laboratory Work

In the laboratory, the basis for the function of measurement was illustrated by weight measurements with an analytical balance and volume measurements with the buret and pipet. Many of the teachers found the use of a good analytical balance a new experience. Other types of measurements were illustrated by experiments with the *p*H meter, the refractometer, the Du-Nouy tensimeter, the viscosimeter, the polarimeter,

the spectrophotometer, and the conductance bridge. The second function, that of analysis by both chemical behavior and physical measurement, was illustrated by experiments in semimicroqualitative identifications and separations using thioacetamide and the West non-sulfide scheme, paper chromatography, electrodeposition of copper from a coin, refractive index, alcoholic content of a beverage, and microscopy. The preparation function of the laboratory was limited to relatively few examples, which included the preparation of inorganic paper chromatograms, certain colloidal systems, and inorganic crystals. Also, certain solutions had to be prepared.

The Fellows were divided into three sections of about eight persons each, with some meeting in the morning and some in the afternoon. They were given a list of about a dozen selected experiments and were permitted to select those that they found to be new or of particular interest. Since there were about ten actual laboratory periods for each person, a maximum of seven to nine experiments could be performed. Many of these could be done in a single period while others were extended through several. Working in pairs was permitted in some cases. The experiments were staggered so that for a single laboratory section as many as six or seven different experiments were in operation at one time. Mimeographed directions for the experiments were given in a short outline form, together with library references. Detailed directions were purposely avoided so that questions and discussions between instructor and student developed personal relationships. A written report, which involved a considerable amount of library work, was required for each experiment.

Inspection Trips

For the bi-weekly inspection trips, the combined chemistry and physics groups were conveyed by special busses to the particular facility visited. One of these was an all-day trip to the Pittsfield, Massachusetts, operation of the company. These trips furnished opportunity for a first-hand knowledge and appreciation of the nature and operation of a large industrial organization. Both research and manufacturing operations gave a better reality to the application of science. To see the operation of a mass spectrometer or an electron microscope was a unique experience.

Other Features of the Program

While the academic credit for the course was optional, very few Fellows in the later years of the program failed to work for a grade. In the early years grades were given on the basis of written examinations at the end of the program. Because of the lack of a text and the diverse nature of the subjects covered, a substantial number of the Fellows decided not to risk the chance for a poor grade, while the others spent an uneasy several weeks in an undercurrent of tension. The problem was finally resolved by basing the grade for the eight A.M. lectures on the quality of the notebook writeup for these lectures. The grade for the 9 A.M. lecture-lab course was based on the laboratory reports, together with a written examination on the work of the classroom. For the latter, a group of questions was distributed about four days before the examination and the examination itself was made up of a selection from these. The result was that study and discussion groups were organized with the Fellows teaching each other.

An important feature of the program was the coherent social group developed, where much could be learned from a free exchange of ideas. In the selection of the group, an attempt was made to obtain a nearly equal balance between men and women in different age groups, years of experience, and geographical location. The Fellows were required to live together in one of the dormitories and to eat together in the College dining hall. The director and teaching staff made it a practice to eat lunch with the group. Families were not permitted. Weekends, from Saturday noon, were free for recreation. Many remained at the College to catch up on their work. Others found recreation in visiting nearby areas of interest or returning to their homes, where possible, for family visits.

Group sociability was accomplished by committees of the Fellows which planned Friday evening and weekend recreation. This varied from week to week and took the form of picnics, parties, and baseball games.

Two or three special off-campus dinners, as well as an equal number of on-campus dinners or luncheons, were high lights of the program. At each of these, a talk concerned with some subject of company interest was given by an official of the company.

Representatives of the Educational Relations Service of the company met with the group on several occasions to discuss the educational materials that were available from the company. At the beginning of the program, this Service gave each Fellow a personalized notebook, and at the end presented to each a special Fellowship emblem.

A continuing contact was made with each Fellow through the publication called "The GESF News." The College also inscribed the name of each Fellow in the record of alumni. Many well-qualified students have been recommended to the College by their teachers who attended this summer institute.

Over the years, the participants have, in general, evaluated the program with enthusiasm. While for most it was a period of concentrated hard work, yet it was one of great personal satisfaction. In the friendly atmosphere, difficulties were accepted with good humor and a fine spirit of conscientious effort. There was a close relationship between the staff and the Fellows.

It is believed that the success of the program was the result of experience gained over many years of operation. The College staff learned to adapt itself to an understanding of teachers' problems, which are somewhat different from those of college students. The teachers were eager for specific backgrounds that would be of direct value to them in their classroom teaching. The program was evaluated each year in conferences between the staff and representatives of the company. Consideration was given to the written criticism and comments that were obtained each year from the new group of Fellows. New ideas were introduced as the personnel of the staff changed over the years. The program ended in an era of awakened attention to better science instruction.

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Abbreviations in Russian Chemical Literature

As in other languages, official abbreviations are used in Russian chemical literature, sometimes with lapses from good form or clarity. Unofficial specimens crop up in somewhat the same free-wheeling fashion as in English-language publications. Authors abbreviate terms, ordinarily spelled out, if they recur often in the text of a paper. It is good form in such cases to follow the first occurrence of the complete term with the abbreviation in (), then to abbreviate all recurrences. It is bad form to abbreviate with no explanation. Use of abbreviations common to literature in general is acceptable both in English and in Russian. *Chemical Abstracts*, in a footnote to its list of abbreviations, mentions approval of this practice. Its counterpart, *Referativnyi Zhurnal Khimiya* (*RZ:Kh*), voices neither approval nor disapproval, beyond including some familiar general entries in its approved lists.

The foremost source of official sanction is *Vsesoyuznyi institut nauchnoi i tekhnicheskoi informatsii* (All-Union Institute for Scientific and Technical Information, VINTI), an affiliate of the Akademiya Nauk SSSR (Soviet Academy of Science). Other units of the Academy may participate, as may any of the other four Soviet academies of science. Those most directly interested are Akademiya Meditsinskikh Nauk SSSR (AMN) (medicine) and Vsesoyuznaya Akademiya Selskokhozyaistvennykh Nauk imeni Lenina (VASKhNIL) (agriculture). Publishing houses have their own standards, official only for their own publications but often having wider acceptance.

The abbreviation style which joins initial and final letters is much commoner in Russian than in English, and indicates the hiatus by a hyphen instead of an apostrophe. Some examples approved by *RZ:Kh* are к-а (кислота, acid), р-р (раствор, solution), д-р (доктор, doctor), and В-во (Вещество, compound). The final letters are variable because they follow case endings; thus, р-р may become р-ру. Again, т-ра (for temperature) may appear as т-ре or т-ру, but is shortened to т. when followed by a modifier (e.g., for boiling, melting, decomposition, or absolute).

Chemical literature in Russian uses two different alphabets, Cyrillic and Roman, for scientific terms and abbreviations. Latin names of plants, animals, and microorganisms, and abbreviations formed from them, are printed just as in Western European literature. Borrowed scientific terms (taken more commonly from English than from German or French) often get the same treatment. Thus, BCG appears regularly for bacilli Calmette-Guerin although its Cyrillic counterpart, БЦЖ, is in the approved list. Again, RNA (for ribonucleic acid) is nearly as common as РНК (for the Russianized name). Some much-used numbers are symbolized in Roman type, e.g., Re = Reynolds no., Nu = Nusselt's no., Pr = Prandtl's no. Some English-language number-and-letter combinations have been borrowed, e.g. 2,4-Д and 2,4,5-Т for di- and trichlorophenoxyacetic acids, respectively.

As in English, conventional style in Russian literature uses periods and spaces; but the alphabet-soup style is also popular. Thus СССР (Soyuz Sovetskikh Sotsialisticheskikh Respublik, Union of Soviet Socialist Republics) appears in many places including sweaters of Winter Olympics athletes, which gave many American TV viewers their first glimpse of USSR from the grass roots. More pertinent to chemical literature are ТЭС (tetraetilsvinets, tetraethyllead); ВТК (vyazkostno-temperaturnyi koeffitsient, viscosity-temperature coefficient), and АДФ (adenosindifosfat). Accidental formation of an English word sometimes occurs, e.g. OMEN for Otdelenie Matematicheskikh i Estestvennykh Nauk (Division of Mathematical and Natural Sciences), a unit of Akademiya Nauk SSSR, and GET for Gosudarstvennyi elektrotekhicheskii Trest (State Electrotechnical Combine).

Abbreviations of units and quantities, almost invariably in the metric system, use the Cyrillic and Roman alphabets selectively. Many of the names were Russianized from the same Latin or Greek sources or from the same names of discoverers from which they were taken into Western European languages. Greek-letter prefixes are common, e.g., α,β, etc. for position designations, γ for microgram or gamma, and μ for micro- or micron. The symbol ‰, per mil, is used much oftener than in English.

Approved abbreviations in Roman type include °C. and °K. (temperature); °E. (Engler viscosity); °Bé (Baumé scale); Å Ångstrom; d-, l- and dl- as in English but with no distinction from D- and L- for sugar families; R for radical; X for halogen or other unspecified substituent; r for X-ray (roentgen); rad for radiotherapy unit; $n^{25}D$; d^{224}; *p*H; rH; and g for acceleration due to gravity, distinguishing it from Г for gram.

Editor's Note

The manuscript of this paper included as an appendix a series of abbreviations "selected from many which will not be obvious to readers whose Russian is less than fluent. The list is far from exhaustive, but readers who possess an active imagination will find in it some helpful leads toward understanding other abbreviations." Interested readers are urged to request a copy of this list from the author.

Presented before the Division of Chemical Literature at the 137th Meeting of the American Chemical Society, Cleveland, April, 1960.

Some which blend Cyrillic with Greek or Roman type are Mμ (millimicron); μa (microampere); р/час (roentgens/hr); спирт-ОН (alcoholic OH). Symbols for chemical elements, and formulas derived therefrom, are international and are used in Russian just as in Western European languages. This may even apply to the recent change of argon from A to Ar, but perhaps not yet; progress of changes in chemical and biochemical nomenclature from West to East has often been no faster than from East to West.

Combining symbols or abbreviations into words is a trick not limited to any one language. The alloy names alni (Al:Ni) and alnico (Al:Ni:Co) have been Russianized, and there are other chemical examples. Soviet literature uses this trick with exceptional freedom in forming short names from long designations for publishing houses and other organizations. Many are familiar in Roman type from Soviet publications issued in Western European languages and in English translations, now widely circulated, of Russian scientific and technical articles. Some examples are Goskhimtekhizdat (Gosudarstvennoe khimiko-tekhnicheskoe izdatel'stvo, State Chemical-Technical Publishing House); Gosplan (Gosudarstvennaya planovaya komissiya, State Planning Commission); GosFizKhim (State Physicochemical Institute); Mostekhfilm (Moskovskaya studiya tekhnicheskikh filmov, Moscow Technical Film Studio).

In general, Russian indulges more freely than does English in certain tricks of abbreviating words and terms, and is liberal but judicious in choosing between Cyrillic and Roman type. Similarities in practice are numerous; official approval is accorded in editorial offices for similar reasons. In the Soviet Union the approving bodies are necessarily government organization; academies, ministries, institutes, and universities make the decisions for their own publications. Unofficial choices are common in Russian as in English; and editors (regardless of language) have about the same troubles with errors, inconsistencies, style fluctuations, unexplained abbreviations, and that ubiquitous imp, the typographical error.

In its printed instructions to abstractors, VINTI uses parallel *Do* and *Don't* columns for guidance in the proper use of commonly used terms and abbreviations. The listed abbreviations are official for VINTI publications and are widely accepted, though not obligatory, by others of the many publications issued by Akademiya Nauk SSSR. English-speaking chemists who learn to read Russian can learn without great difficulty to cope with the abbreviations widely used in chemical and biochemical literature. For the extremely condensed style of the abstract journals, e.g., *RZ:Kh*, readers will need to study the approved lists.

Special attention is given here to the abbreviation practices of VINTI since it occupies such a dominant position as the producer of *RZ* in all its 13 sections. As an affiliate of Akademiya Nauk SSSR it omits clinical medicine from its subject coverage because AMN SSSR has its own abstract journal. Agriculture is treated lightly in deference to VASKhNIL, but the 13 *RZ* sections have so many interests in common with agriculture that many pertinent abstracts appear in at least one *RZ* section.

For chemistry the most pertinent sections are *RZ:Kh*, which now has separate issues for general and organic chemistry, *Biologicheskaya Khimiya* (*RZ:BKh*) and *Biologiya* (*RZ:B*) for biological chemistry and biology respectively. Instructions to abstractors and editors were issued in 1957 (*RZ:Kh*), 1958 (*RZ:B*), and 1959 (*RZ:BKh*). They are supplemented at irregular intervals by printed letters of instruction. Press runs have been small (*RZ:Kh* 400 or 500, *RZ:BKh* 1000, *RZ:B* 4000 copies), so there is little distribution outside of the USSR.

Abbreviations for *RZ:Kh* are classified thus:

Languages (for bibliographic references).
Patents (sources).
Words and terms.
Measurements, units, symbols (subclassified by fields).

The list for *RZ:BKh* refers to the *RZ:Kh* list and classifies its own entries simply as "Words and Terms" and "Measurements, Units, Symbols" (subclassified). The list for *RZ:B* has another classification:

Words commonly used.
Scientific names and terms.
Metric units (conversion table from nonmetric units).
Measurements, units, symbols (subclassified).
Soviet republics.
Soviet academies and institutions.

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More Mnemonics

For the electronegativity series of the elements most often encountered in a general organic chemistry course, F O Cl,N Br C,H:

For Our Clambakes, Never Bring Canned-Ham

(The punctuation marks after Clambakes and Canned indicate approximately equal degrees of electronegativity.)

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Proceedings of the

California Association of Chemistry Teachers

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The General Philosophy of Organic Nomenclature

Organic chemists have been striving for systematization of nomenclature ever since the appreciation of homology and isomerism. When it became evident that the term *alcohol*, for example, represented not only a compound (grain alcohol) but also a family, a "system" came into being designed to name the members: methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, etc. Isomers demanded subdivisions, as *n*-propyl and *i*-propyl alcohols. Four prefixes were found for the four butyls, but the pentyls, hexyls and higher radicals became so unwieldy that other systems had to be invented. Many of the early plans for naming compounds, although inadequate for complex examples, have become so thoroughly entrenched that they continue to be used. This should make any chemist pause before starting some new system, for experience shows that even if such a system were to enjoy some acceptance, it is highly unlikely that it ever would replace the other systems. Instead, it would merely expand the existing *n* systems to "*n* + 1" and give rise to more complexity rather than to simplification.

It may be helpful to list the more important plans of nomenclature that have been used: (1) the simple nucleus plan, or the smallest significant nucleus, such nuclei being carbon in triphenylmethane, silicon in dimethylsilane, C-OH in methyldiethylcarbinol, C-CHO in trimethylacetaldehyde, C-COOH in phenylacetic acid, and other small nuclei; (2) the complete skeletal plan, or the largest significant nucleus, which includes all trivial names (as vanillin, chloral, cholesterol, oleic acid) as well as some with structural adaptations (as isophthalic acid, neopentane); (3) Geneva system; (4) IUC rules (*1*); (5) IUPAC rules (*2*) continuing since 1949; (6) various devices for handling certain kinds of structures, as bicyclo names or spiro names; (7) additive names, as 2,3-naphthalenedimethanol or 9-fluorenepropionitrile; (8) fused ring systems (*3*) as pyrido[2,3-g]quinoline; (9) "a" names, as 3,7,11-trioxa-1-dodecanol, 2,7,9-triazaphenanthrene; (10) *Chemical Abstracts Index* usage (*4*), which represents the choice for indexing purposes of the editors of *C.A.* among the various systems, usually from one Decennial Index to the next; (11) British usage (*5*) or the style favored by the editors of *J. Chem. Soc.*

It is not the purpose of this paper to develop details of any of the above systems or plans. Rules for them can be found elsewhere. Instead, it aims to present underlying principles of nomenclature that are basic to all of the systems.

Classification

First in the naming of any compound is the requirement of classification. Once classified, the substance then must be named in conformity with rules governing the class in the system chosen. Thus, CH_3OH is named methyl alcohol or methanol because it classifies as an alcohol. It would be wrong to call it hydroxymethane since alcohols are not named as hydrocarbons.

Inspection of the structure $CH_3—O—COCH_3$ shows it to be an ester; hence, ester rules apply and the name

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EDITOR'S NOTE: At one time or another every chemist finds that he needs assistance in a nomenclature problem and he often discovers others are as much in the dark as he is. Too often a chemist will assume that he knows the rules of nomenclature and will devise a system which he is confident will fit into one of the standard systems, when actually it does not. It may take a rather rude awakening to realize that there are established systems and also that no single one can be applied universally. As with language, there is no simple "Esperanto" with a single set of rules that meets all situations. A person with some knowledge of nomenclature probably will discover that the literature and textbooks are cluttered with misinformation. Even authors of papers submitted to research journals may be dismayed to find referees united in opposition to correct nomenclature because they have not encountered the situation before.

With this in mind, Professor Charles D. Hurd of Northwestern University was asked to prepare a paper on organic nomenclature in view of his experience in this field. He is a member of the ACS Nomenclature Committee. He has served on the ACS Organic Division Nomenclature Committee for three decades, and was the first chairman when it was started in 1930. From 1939 to 1944 he was chairman of the Carbohydrate Nomenclature Committee which at the time was sponsored jointly by the ACS Divisions of Carbohydrate Chemistry, Biological Chemistry, and Chemical Education. This Committee was active in formulating rules for carbohydrate nomenclature. Dr. Hurd has been a member of the Nomenclature Committee of the National Research Council since 1938 and was its 1958–60 chairman.

One might question the listing of this paper under the CACT Proceedings, but without stretching things too far it was agreed that this paper could be so classified since Dr. Hurd has on two occasions been associated with California teaching: once as visiting professor at University of Southern California and once as a lecturer at a summer organic symposium at Stanford University.

The CACT Editor acknowledges his great debt to Dr. Hurd for his friendly counsel and helpful advice on many occasions. It is hoped that all readers of these pages will derive a great deal of pleasure from reading and applying this material.

JOHN L. ABERNETHY
Editor, CACT Proceedings

is methyl acetate. An erroneous classification as an ether would lead to the name methyl acetyl ether. The compound p-$CH_3C_6H_4NHCOCH_3$ is an amide, not an amine, correct names for it being aceto-p-toluidide or N-p-tolylacetamide. A name N-acetyl-p-toluidine follows an erroneous classification as an amine.

If the compound contains two or more functions, one of these must be selected as the principal function. Thus, $CH_3CHOHCH_2COCH_3$ is both and alcohol and a ketone and either could be selected as the principal function; in practice the ketone is usually given the preference.

Number of atoms

To be correct, the number of atoms required by a name must be no more or no less than the number of atoms of the compound. Thus, the name ethyl acetate calls for four carbons, two for ethyl and two for acetate. Similarly the name triphenylcarbinol specifies 19 carbons (18 for the three phenyls and one for carbinol), agreeing with the structure. In contrast, the name "3-thiophenealdehyde" designates 4 carbons (4 for thiophene and none for aldehyde); hence it is incorrect since the compound C_4H_3S—CHO possesses five carbons. That "aldehyde" carries no carbons is obvious from a consideration of the names of well-known aldehydes. In acetaldehyde, for example, the "acet" (or acetic) designates two carbons. Correct names for the thiophene compound would be 3-thenaldehyde or 3-thiophenecarbaldehyde (a recently approved IUPAC suffix replacing -carboxaldehyde).

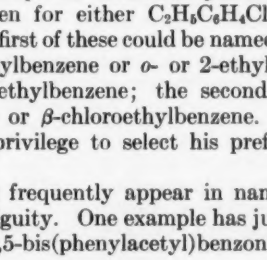
Another indefensible name, less encountered now than two decades ago, is glucosidoglucose for $C_{12}H_{22}O_{11}$ (as maltose). The name should be glucosylglucose. Glucose is $C_6H_{12}O_6$, glucosido is $C_6H_{11}O_6$, and glucosyl is $C_6H_{11}O_5$; hence, glucosidoglucose would call for $C_{12}H_{22}O_{12}$ which is one oxygen too many.

Avoidance of ambiguity

Regardless of which system is selected, no name is good if ambiguous. Bromophenylacetic acid lists the substituting prefixes alphabetically but one is not sure if $BrC_6H_4CH_2COOH$ or $C_6H_5CHBrCOOH$ is in mind; p-bromophenylacetic acid would specify the former and α-bromophenylacetic acid the latter. A simpler, hence better, name for the latter is phenylbromoacetic acid. Changing the order of the prefixes makes it quite unambiguous.

Another example is 2-chloroethylbenzene since this might be taken for either $C_2H_5C_6H_4Cl$ or $C_6H_5CH_2CH_2Cl$. The first of these could be named clearly either as o-chloroethylbenzene or o- or 2-ethylchlorobenzene or 2-chloro-1-ethylbenzene; the second as (2-chloroethyl)benzene or β-chloroethylbenzene. It would be an indexer's privilege to select his preference among these options.

Parentheses frequently appear in names to help in avoiding ambiguity. One example has just been given; another is 3,5-bis(phenylacetyl)benzonitrile to represent



The parentheses emphasize that the phenylacetyl radical is what is taken twice. Use of bis with complex radicals is the same as use of di with simple radicals. Thus whereas it is bis(phenylacetyl) it would be diphenyl or diacetyl. Since di is not written in italics bis should not be either.

Suffix for principal function

Express the principal function (the class of compound) by the ending of the name and avoid multiple suffixes if possible. For example, $CH_3CHOHCH_2COCH_3$ with ketone as the principal function is a pentanone. The hydroxyl group should be designated as a prefix: 4-hydroxy-2-pentanone. The name "4-pentanol-2-one" violates rules in view of the two suffixes. There are names where two suffixes are unavoidable, as 2-pentenoic acid, since here there is no prefix to represent ethylenic unsaturation.

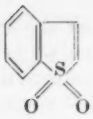
It is not unusual to change the system of naming because of the presence of a function. Compounds $CH_2(C_6H_5)_2$ and $CH_2(C_6H_4SO_3H)_2$ may be used to illustrate. The first is usually named diphenylmethane but the second cannot be called diphenylmethanedisulfonic acid for that would imply $(C_6H_5)_2C(SO_3H)_2$. Instead, the hydrocarbon is renamed as methylenedibenzene for purposes of including the principal function. The name, if the para isomer, would be 4,4′-methylenebisbenzenesulfonic acid.

Spaces in a name?

Many names are correctly written in one word and many others in two or more words. Ethylbenzene is correct without a space whereas ethyl alcohol requires the space. What governs such matters? A simple device (*6*) is the following: In both of the compounds listed, $C_2H_5C_6H_5$ and C_2H_5OH, the ethyl group may be considered as replacing a hydrogen in a fundamental compound, H—C_6H_5 and H—OH. Ethylbenzene is a one-word name since "benzene" is the name of the fundamental compound and unchanged by substitution of ethyl. Ethyl alcohol is a two-word name since "alcohol" is not the name of the fundamental compound H—OH. Instead it is water. If someone once had popularized the name of "ethylwater" for this beverage then it would have been correctly listed with no space in the name.

Ketones and ethers are two-word names if symmetrical and three-word names if unsymmetrical for the same reason. "Methyl ethyl ketone," Me—CO—Et, may be stripped back to the fundamental unsubstituted compound H—CO—H but this is no longer called "ketone"; hence the 3-word name. Chemists have purposely avoided the name "methylethylformaldehyde" but if such a name had been used it would have been a one-word name. Similarly, butyl propyl ether is a three-word name since the fundamental unsubstituted compound, H—O—H, is not named ether.

Sulfides, sulfones, sulfoxides, acetals, acid anhydrides, glycosides also have spaces in the names, as methyl sulfide, propionaldehyde ethyl acetal, formic acetic anhydride, and methyl xyloside. Sulfones sometimes are named as dioxides. Thus,



is benzothiophene 1,1-dioxide. Since oxide and dioxide always are separate words in other areas of chemistry they should be separate words in this area. The style "benzothiophene-1,1-dioxide," therefore, should not be used. Pyridine N-oxide is another example.

Amines are one-word names since "amine" is regarded as a contraction of ammonia and hence is used as the root to which the name of a substituent is directly attached as prefix: methylamine, not "methyl amine." Other comparable root substances as arsine, hydrazine, and toluidine follow this treatment regularly: phenylarsine, 2,4-dinitrophenylhydrazine, *o*-chloro-*p*-toluidine.

Acids, salts, and esters are two-word names, paralleling inorganic terminology: sulfuric acid, hence malonic acid; hydrogen chloride and silver chloride, hence hydrogen acetate, lithium acetate, and ethyl acetate.

Occasionally one meets a person who desires to split up a one-word name "to make it more understandable," as "*p*-nitro phenyl hydrazine." Since this violates an accepted principle it cannot be countenanced, but the end may be achieved (if desired) by use of hyphens, as *p*-nitro-phenyl-hydrazine, since the hyphens keep it as a one-word name.

Another error frequently encountered is contraction of a two-word name to a one-word name. An obvious error is "methylethyl ketone." Another is the use of "orthoesters" for ortho esters, or "chloroacids" for chloro acids. A little thought will show why this is indefensible. An ortho ester that may have been in mind is orthoacetic ester. Obviously, the two-word expression should not become one-word by deletion of "acetic." Similarly, "chloro acids" might include chloroacetic acid, chlorobenzoic acid, etc., which are all 2-word names.

Naming substituents

There is no problem if the substituent is to be part of a one-word name with that word retained in the name. It is directly attached, as in chloromethane, chlorobenzene. A problem does arise, however, if the substituting group entered a compound with a two-word name. Compounds CH_3OCH_3 and CH_3OCH_2Cl are illustrative. The former is a symmetrical ether, named methyl ether. The latter is a hemiacetal chloride (the chloride of CH_3OCH_2OH) but this class may be named as an ether. As such it is a mixed ether calling for a three-word name, methyl chloromethyl ether. To name it "chloromethyl ether" as is sometimes done is unjustifiable, for this two-word name would represent the symmetrical compound $(ClCH_2)_2O$.

It might be pointed out that CH_3OCH_2Cl could have been named chloro(methyl ether), although no one does so. In this form chloro modifies the whole compound, not simply the methyl group. The situation is comparable to $2a + b$ and $2(a + b)$ in algebra.

Mustard gas, $(ClCH_2CH_2)_2S$, is another compound causing trouble in naming. It is a symmetrical sulfide, hence a two-word name. The group occurring twice is β- or 2-chloroethyl and the name is simply 2-chloroethyl sulfide (or bis-2-chloroethyl sulfide). Contrast this name with β,β′-dichloroethyl sulfide which appears so frequently.

Another place of trouble in two-word names is the location of substituents and symbols. They must be attached to the term they are supposed to modify. Of these two names methyl α-D-glucoside and α-methyl D-glucoside, the first is correct and the second is not since α refers to the glucoside part of the name rather than to the methyl. Other examples are ethyl chlorobenzoate, 2-chloroethyl benzoate, methyl 4,6-isopropylidene-β-D-glucoside.

Punctuation in a name

Commas (and sometimes colons) are used to separate like things as 2,4,6- or α,β-, or 2,3:4,6-; hyphens to separate unlike things as α-D- or 2-chloro; and parentheses to collect complex terms so as to avoid ambiguity, as 2,4-bis(chloromethyl)benzaldehyde.

Designation of valence

In salts, esters, ethers and other two-word names the quantity factor of one word may be implied by the valence requirement of the other word. Compounds such as Na_2CO_3, $FeCl_3$, K_2O are familiar inorganic examples, customarily named sodium carbonate, ferric chloride (or "iron(III) chloride" in the to-be-preferred stock system) and potassium oxide rather than disodium carbonate, ferric trichloride, or dipotassium oxide. Since carbonate is bivalent it calls for two sodiums whether expressed or not.

Similarly, ethyl ether is as correct as diethyl ether, considering the bivalent requirement of the word ether. Sodium succinate is correct for $NaOOC(CH_2)_2COONa$, the acid salt being sodium hydrogen succinate. Ethyl malonate and ethyl hydrogen malonate are illustrative for esters and acid esters. The term diethyl malonate is not incorrect but is no more correct than the shorter term ethyl malonate.

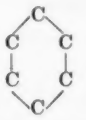
Prefixes

Three broad classes of prefixes call for comment: substituting, structural, and operational prefixes. Common substituting prefixes include chloro in chlorobenzene, nitro in nitromethane, and many others. Rules are open regarding the sequence of two or more such prefixes for they may be listed either alphabetically or in order of increasing complexity, but they should always be directly attached to the parent name.

Structural prefixes are used to distinguish among isomers. They include *anti*, *cis*, D *endo*, *erythro*, *exo*, *gluco*, *iso*, L, *meso*, *meta*, *neo*, *normal*, *ortho*, *para*, *secondary*, *symmetrical*, *syn*, *tertiary*, *threo*, *trans*, *vicinal*, *xylo* and many others having to do with arrangement of atoms. These are generally attached to the name by a hyphen (iso and neo being exceptions in *C.A.* usage) and are set off from the name by different type (as italics). The adjective form of these may be used alternatively, in which usage they are no different from other adjectives: they are spaced from the name and set in ordinary type. Examples of

prefix form, unabbreviated: *meta*-xylene (not "met-axylene"), *tertiary*-butyl, *normal*-pentyl, *cis*-2-butene, L-*threo*-2,3-dichlorobutane (but neopentane, isobutyl). Examples, abbreviated: *m*-xylene, *n*-pentyl, *tert*-butyl or *t*-butyl, *i*-butyl. Examples of the adjective form: meta xylene, cis 2-butene, trans olefins, normal pentyl, tertiary butyl, syn oximes, syn benzaldoxime.

Operational prefixes tell of a chemical change, direct or indirect, on the root name, thereby creating a new nonisomeric root name. An example is "cyclo" in cyclohexane, wherein the CCCCCC of hexane has been altered to become



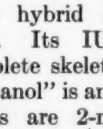
An operational prefix never should be separated from the root name it modifies, nor should it be set in different type. Thus, one would say nitrocyclohexane but never cyclonitrohexane. Other operational prefixes are *aza*, *bicyclo*, *dehydro*, *deoxy*, *homo*, *hydro* or *hydr*, *nor* and *bisnor*, *oxa*, *pyro*, *thia*. For alphabetical indexing purposes none of these prefixes should be alphabetized with substitutional prefixes.

Hybrid names

It is unjustifiable to use a name derived partly from one system and partly from another. The compound $(CH_3)_2C{=}CH_2$ is illustrative. Its complete skeletal name is isobutylene. Its simple nucleus name is *unsym*-dimethylethylene, and its IUPAC name is methylpropene. Obviously, "isobutene" is in none of these systems and should never be used. "Isopropanol" is another hybrid name that is particularly troublesome. Its IUPAC name is 2-propanol and its complete skeletal name is isopropyl alcohol. "Tertiary butanol" is another offensive name, for its correct names are 2-methyl-2-propanol, *t*-butyl alcohol, or trimethylcarbinol.

Miscellaneous things to avoid

The delta to locate a double bond. At one time this was used freely to indicate unsaturation, as Δ^2-cholestene or Δ^3-hexene. Since these names mean the same as 2-cholestene or 3-hexene it is evident that Δ serves no purpose. Occasionally Δ is useful and is employed correctly, as in naming doubled cyclic systems having ethylenic unsaturation at the juncture; e.g., $\Delta^{9,9'}$-bifluorene, or $\Delta^{2,2'}$-biindoline. Also, Δ is helpful in naming the dihydroazoles, as Δ^4-thiazoline for



The distinction between ester and acid ester, salt and acid salt. Sodium sulfate and sodium tartrate are salts, whereas sodium hydrogen sulfate and sodium hydrogen tartrate are acid salts. Similarly, ethyl hydrogen tartrate is an acid ester. One should use care, therefore, to avoid the expression "acetic acid ester," for acetic acid has no acid ester. "An ester of acetic acid" is the expression to use.

"Tosylate" as a noun. Although tosyl is an acceptable abridgment of toluenesulfonyl and although the verb "to tosylate" follows logically, there is no support for "tosylate" as a noun. One should not say "the tosylates of various alcohols" or "preparing tosylates as derivatives" any more than "acetylates" for acetates or "benzoylates" for benzoates. There is no such thing as "tosic acid" or "tosylic acid" hence the proper term for the salts and esters under discussion is "toluenesulfonates."

Faulty numbering of alkyl radicals. Since the position of attachment of an alkyl radical to a nucleus is No. 1, it is always unnumbered; thus butyl or *n*-butyl but never 1-butyl. Substituents on the radical are numbered even if they are on this No. 1 carbon; e.g., 2-chloropropyl for $CH_3CHClCH_2$-. Alkyl substituents are treated no differently. The *sec*-butyl radical, $CH_3CH_2\underset{|}{C}HCH_3$, is named systematically as 1-methylpropyl. It is incorrect to refer to it as "2-butyl." The group $CH_3\underset{|}{C}HCH_2CH_2CH_2N(C_2H_5)_2$ is 4-diethylamino-1-methylbutyl.

New trivial names. It is unavoidable that compounds of unknown structure be given trivial names. All compounds of the early days were in this category as are many natural compounds of recent times. The situation is quite different, however, when a new compound of known structure, which is amenable to systematic nomenclature, has been synthesized. A systematic name should be assigned. Chemists can be thankful that this is usually done but occasionally one encounters such needless names as triptane, triptycene or barrelene which are undecipherable unless memorized. Their systematic names—trimethylbutane, 9,10-dihydro-9,10-benzenoanthracene, and bicyclo[2,2,2]-octa-2,5,7-triene—may be a little longer but this is of no consequence considering the few times these compounds are apt to be referred to in the literature. The systematic names give the reader a chance to develop and understand the structure.

Conclusion

In closing, it may be well to recall the story of the magpie who was teaching the assembled birds how to build nests. The magpie was holding forth in his inimitable style to an attentive audience. Then one bird rustled his feathers and flew away, being satisfied that he could make his nest. Another bird left and another until no bird remained at the end of the lesson. Indeed the other birds did build nests, but not magpie nests. In the world of birds this may be all to the good.

Possibly many chemists have considered it a rather dreary business to study rules of nomenclature. So, like birds, they may have left the study long before its completion. As a matter of fact, the twittering that goes sometimes for nomenclature is indeed for the birds; but in all seriousness, rules are available and do deserve serious study. The following partial bibliography will give adequate guidance for most situations.

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A Summer Chemistry Program for Teenagers

Teaching chemistry in terms of modern orbital theory to about 300 youngsters, 11–17 years old, was a summer project in 1959 and 1960 for a group of undergraduate and graduate students at the University of California. The enthusiastic approval of the participants and interested adults in the San Francisco Bay area indicates that a similar program could be successfully carried out in many other areas of the country. The comparative youth of the sponsoring group, and consequent lack of experience in the teaching field, was unusual in a program of this size and suggests the wide variety of groups which might launch such a program elsewhere.

Members of Sigma Chapter of Alpha Chi Sigma, a national professional fraternity in chemistry, planned the program originally to help a small group of boys fulfill the requirements for the Boy Scout Merit Badge in Chemistry. The enthusiasm of the Scouts led the fraternity members, supported by the chapter faculty adviser, to realize the importance of a second goal in developing the project—interesting the Scout age group in further exploration into chemistry.

Chemistry was introduced to the teenagers in a series of eight meetings on successive Saturday mornings during July and August. A typical session included a half hour test, an hour lecture, and 90 minutes of laboratory work. The test and lecture were conducted with the entire group, which then separated into groups of about 20 for the laboratory experiments. Home assignments were an integral part of the course. A short paper on some aspect of chemistry assured some exposure to general scientific literature; freedom to choose his topic allowed each individual to explore an area of particular interest to himself. Each participant was required to present for approval a collection of chemicals found in the home, together with their correct chemical formulas. Finally, an optional home experiment was assigned at each session for those who wished to receive extra credit.

Classroom Work

The topics discussed were Atomic Structure, Periodic Table, Bonding, Metals, Non-Metals, Organic Chemistry, and Solvents. At the eighth meeting a final exam was given over the seven lectures.

In the first lecture, the statistical nature of the electron was presented and the weaknesses of the planetary model of the atom was discussed. The concept of spin was introduced as an important atomic force. Spin and other forces were clarified by introducing the principle of minimum energy. Test results showed that this lecture was very successful in teaching these relatively new concepts.

Succeeding lectures were designed to make use of the ideas presented in the first. The periodic table was derived from an energy level diagram. Bonding was explained in accord with the orbital model, and balloons were used extensively as visual aids. Lectures on metals, non-metals, and carbon chemistry included the use of oxidation states and demonstration of the activity series.

Laboratory Experiments

All but two of the laboratory experiments were designed specifically for the course. Equipment required for each student was one beaker, six test tubes, 12 in. of glass tubing, two rubber stoppers, one small (250 ml) Florence flask, and a Bunsen burner. Everything except the glass tubing and four test tubes could be cleaned and returned to the stockroom.

The instructors chose spectacular experiments to make a strong impression and lead to a desire for further investigation. The instruction sheet for each experiment explained the purpose and the mechanism relating it to the lecture material. Suggestions for further experimentation were often included.

The laboratory experiments that best reinforced the lecture material and prompted enthusiastic comments from the classes included:

Non-aqueous displacement of lead by aluminum foil when the foil was put into molten lead chloride

Preparation of silicon hydride by the interaction of magnesium and silicon on the addition of hydrochloric acid—the silane formed then ignited on contact with air

Preparation of a urea-formaldehyde plastic

Preparation of aluminum iodide by heating aluminum foil with iodine crystals (the compound formed was then reacted with water)

Preparation of ammonium amalgam and sodium amalgam

Home Experiments

The series of home experiments was chosen to utilize household products or easily obtainable chemicals and makeshift apparatus, yet to be as vivid and pertinent to course material as possible. The instructions for these experiments included the theory involved and suggestions for further study. To receive credit, the young student was required to produce yield data on his experiment.

Six experiments were presented:

Boron oxide from pyrolysis of boric acid

Hydrogen, collected in balloons, from the reaction of aluminum foil in muriatic acid

Iron (III) chloride from burning of steel wool in chlorine, the chlorine to be prepared cautiously by acidifying liquid bleach

Copper (I) sulfide from the interaction of copper wire and sulfur, including testing the conductivity of both copper and copper sulfide with a train transformer

Formaldehyde "clock" reaction from the autocatalytic oxidation of formalin by liquid bleach, including determination of the rate law for the reaction

Chloroform from the oxidation of rubbing alcohol by liquid bleach using baking soda as a buffer

Safety

It has been mentioned that "spectacular" reactions were used for greatest impact. Obviously, the hazards involved had to be thoroughly explained. Safety rules were pointed out at the beginning of each laboratory period and repeated in the printed instructions. Not even a burn or cut occurred; it is believed that the boys gained an increased awareness of the danger of unsupervised and haphazard experimentation.

Evaluation of the Program

The first summer, 120 boys enrolled and 70 successfully completed the course. The second summer, the course was opened to any boy or girl from 11 to 17, and 170 boys and three girls enrolled. Most still were Scouts who wished to fulfill the merit badge requirements. The weekly attendance averaged 120; interest remained high and more than 100 boys received merit badges. Points were assigned for each experiment, test, and special requirement; passing score was taken as 500 of the total 1000 points possible, with a certain minimum of participation required in both experimental and academic phases.

On the basis of expenses incurred the first summer, one dollar was charged each person enrolling. The fee covered the cost of paper, merit badge booklets, chemicals, and breakage fees for equipment borrowed from the University. Actual expenses exceeded the money collected by a small amount; this deficit was underwritten by two local professional societies and, in the first year, by the area Scout councils.

The paper work involved was handled by the fraternity members involved in the course, except for actual mimeographing of stencils. Preliminary publicity releases were prepared and sent to local newspapers and Scout councils in June. During the course, brief résumés of each lecture were distributed weekly. Instructions for laboratory and home experiments were also given to each student at the beginning of the appropriate laboratory period.

It should be noted that no more than nine persons were involved at the instruction and supervisory level. Each of these men was in charge of one laboratory section or helped to distribute supplies from the stock room; three also took turns preparing and delivering the lectures; the entire group cut stencils, marked tests, and recorded grades.

Interestingly, the course was begun, developed, and carried to completion by a comparatively young group, from 18 to 23 years old. The first year all but one of the fraternity members involved had just completed the junior or senior year, and one had completed his first year of graduate study. The following year five of the laboratory instructors were first and second year graduate students and four were undergraduates, including one who had just completed his freshman year. The youth of the sponsoring group was felt to be an asset in building rapport with the Scouts; the small age differential (3–12 years) between "teachers" and "pupils" perhaps encouraged the natural inquisitiveness of the Scouts with less effort than older instructors would have required. In any case the infectious enthusiasm of the sponsors was one of the most important factors in the presentation and reception of the program.

A group of some 20 Scouts from the first year program were invited to continue meeting on Saturdays during the ensuing fall semester, with three of the fraternity men. The advanced program had two objects: to train laboratory assistants for the course to be given the following summer, and to stimulate and channel the special interests of these students. The "laboratory assistant" idea was of great aid to the laboratory instructors during the second summer. The total value to the individuals of this select group cannot of course be evaluated; but the continued interest, outside study, and penetrating questions of some of the participants of these completely voluntary sessions were very encouraging.

✦ ✦ ✦

Chem Ed

BOOK REVIEWS

Atoms, Molecules, and Chemical Change

Ernest Grunwald and *Russell H. Johnsen* both of Florida State University, Tallahassee. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1960. xii + 252 pp. Figs. and tables. 16 × 23.5 cm. $6.25.

This text is prepared for use in a one-semester course in chemistry for students not majoring in the sciences. The amount of subject matter has been carefully limited to emphasize depth of understanding rather than breadth of coverage. The treatment of subject matter involves minimal use of mathematics. The descriptive chemistry included is limited to what is required to develop the theme of the book—the structure of matter and the consequences of that structure. This theme is developed partly from the historical approach and partly in terms of the logical requirements of unfolding theory.

The approach to chemistry in terms of kinds of substances, quantitative relationships in chemical change, and energy in chemical change is followed by the kinetic-molecular theory of matter presented as an example of how a model may be developed to clarify our understanding of macroscopic behavior in terms of submicroscopic particles and processes. Considering Daltonian atomic theory and its inadequacies leads to the development of the nuclear concept of atomic structure. The limitations of Bohr theory are used to introduce the electron-cloud concept of orbitals. The arrangement of electrons in atoms is then correlated with the periodic table. Ionic and covalent binding are then discussed with special reference to the geometric relationships of atoms in ionic crystals and in molecules. The changes which molecules undergo in various types of reactions are discussed with examples drawn largely from simple organic and inorganic compounds. Rate of reaction is discussed briefly. The book closes with an historical account of how the proton and neutron were discovered, current ideas about the structure of the atomic nucleus, nuclear reactions, and nuclear energy.

The traditionalists in our fraternity of general college chemistry teachers may be disturbed by the omission of such familiar topics as chemical equilibrium, oxidation-reduction, and the colligative properties of solutions. Should they desire to incorporate these additional concepts in their courses for students not majoring in science, they will find it easy to do so by building on the framework of ideas presented in this book.

The authors have selected an interesting group of chemical concepts and have developed each one with clarity and care. They have presented these concepts in a sequence which leads the student from the concrete to the abstract—from the simple to the complex. The text is well written, adequately but not lavishly illustrated, and printed in a pleasing format. It will serve well as a textbook for the college student who will have but one semester of college chemistry.

EDWARD C. FULLER
Beloit College
Beloit, Wisconsin

Reviewed in This Issue

Ernest Grunwald and Russell H. Johnsen, Atoms, Molecules, and Chemical Change
Leicester F. Hamilton and *Stephen G. Simpson,* Calculations of Analytical Chemistry
Karol J. Mysels, Introduction to Colloid Chemistry
J. C. D. Brand and *J. C. Speakman,* Molecular Structure: The Physical Approach
Charles E. Reid, Principles of Chemical Thermodynamics
A. J. Berry, Henry Cavendish: His Life and Scientific Work
R. Belcher and *A. J. Nutten,* Quantitative Inorganic Analysis
Edward L. Bauer, A Statistical Manual for Chemists
Carl Djerassi, Optical Rotatory Dispersion: Applications to Organic Chemistry
James B. Jones and *George A. Hawkins,* Engineering Thermodynamics: An Introductory Textbook
Milton J. Rosen and *Henry A. Goldsmith,* Chemical Analysis. Volume 12: Systematic Analysis of Surface-Active Agents
Rene Audubert, and *Serge de Mende,* The Principles of Electrophoresis
Lena A. Lewis, Electrophoresis in Physiology
C. B. Anfinsen, Jr., M. L. Anson, Kenneth Bailey, and *John T. Edsall,* Editors, Advances in Protein Chemistry. Volume 14

Calculations of Analytical Chemistry

Leicester F. Hamilton and *Stephen G. Simpson,* both of Massachusetts Institute of Technology. McGraw-Hill Book Co., Inc., New York, 1960. xii + 334 pp. Figs. and tables. 16 × 23.5 cm. $5.95.

The new edition of this well-known book has six pages less than the previous edition, although certain sections have been expanded and sections have been added on thermochemical reactions, reaction rates, and coulometric titrations. To accomplish this necessitated some deletion and/or condensation of the problems, and more extensive use of abbreviations.

The reviewer has used all of the previous editions of this book as sources for supplementary discussions and problems in his classes. For every type of problem in his own "Quantitative Analysis" specific reference is made to the appropriate section in the fifth edition for students who need extra experience. This sixth edition will be even more useful.

Probably few instructors would agree on what the details should be in such a book. Thus, the reviewer would have welcomed mention of the "Graphic Table of Logarithms and Antilogarithms" by La Croix and Ragot, of circular logarithmic calculators, and of the specification of concentration of a solution in terms of grams of solute per gram of solution for titrations with "weight" burets. Problems might well have been included for some of the currently popular organic complexing titrants.

The reviewer does not share the authors' belief in the merits of the normal system of specifying concentration, or chemical reactivity, of titrants. The equivalent masses of sodium carbonate and orthophosphoric acid (page 34) are not invariable quantities. The permanganate ion may take on at least one, three, four, or five electrons, which means at least four different equivalent weights. What is a normal solution of potassium cyanide solution as a precipitant or complexant in the following cases?

$$KCN = Ag = Ag/2 = Ni/4 = 2Cu/7$$

Either the formula-weight (formular) or the titer system avoids such uncertainties, and the simplest calculation of percentage is

$$\frac{\text{Vol. (or mass) of titrant} \times \text{titer (gm)} \times 100}{\text{Sample (gm)}} = \%$$

The ASTM-SAS approved statement of the Bouguer (not Lambert)-Beer relationship is $A = abc$, in which A is absorbance (not optical density). Filter photometer is preferable to "photoelectric colorimeter" because for years the famous Zeiss and Leitz instruments have been visual, and to physicists colorimeters are tristimulus matching instruments.

As before, the reviewer recommends this book.

M. G. MELLON
Purdue University
Lafayette, Indiana

Introduction to Colloid Chemistry

Karol J. Mysels, University of Southern California, Los Angeles. Interscience Publishers, Inc., New York, 1959. xv + 475 pp. Figs. and tables. 16 × 23.5 cm. $10.

It is the purpose of the author to serve "those who wish to acquire a broad acquaintance with colloids and gain an insight into the basic factors responsible for the observed phenomena and for the principal methods of investigation." The level and extent selected are those of the college senior or beginning graduate student, and for a one-semester course. So, it is primarily an elementary text, one for which the required mathematical apparatus does not extend beyond ordinary algebra and geometry, along with the rudiments of the calculus. Even so, it is a book of substance, and the serious student will find plenty of material which will prepare him for a more comprehensive exposition. It gives an excellent mechanistic, kinetic theory description of concepts which at the more advanced level will require arguments which derive from thermodynamics.

The text is based on the thought that although colloid chemistry may require a different emphasis as compared to the more classical physical chemistry, fundamentally colloids are particles just as are small ions and molecules. In briefest general outline the structural elements are introduced, then their behavior is examined when they are subjected to van der Waals forces, gravitational and centrifugal impulses, and electrical fields. The concluding three chapters are devoted to the consideration of optical effects.

In a task of this kind a writer is always faced with the choice of symbols and abbreviations. In this instance Mysels has put to use what was to us, at first, a complicated system which involved Roman, Greek, German, and Italic large, small, and bold-face letters. But, as is noted in quite another connection (page 268), one "should always remember that it is the concepts and their relations which are of primary importance in understanding nature, whereas the names are only a tool for the communication of this understanding."

Already there are available a number of elementary texts devoted to colloid chemistry; a justification for this one is found in the fact that it is different from them. One cannot fail to be aware that in the new book discussions of a number of the traditional subjects have been omitted, while others have been given apt mathematical treatments which are based strictly upon fundamental laws of physics and chemistry. The explanations of behavior in sedimentation, diffusion, Brownian motion, osmotic pressure, viscosity, electrophoresis, and light scattering are really noteworthy in this respect. The book is brightened throughout by an animated style which is characteristic of the author; at times one feels as if he were sitting in his classroom. Here is represented the able teacher, with a sense of humor to go along.

At the end of each chapter one finds a summary, pertinent references, and a set of problems. The problems are well chosen; they are sometimes simple, sometimes more subtle, and on occasion quite difficult of precise answer. In general, there is every indication that much study, planning, and effort has gone into the preparation of this book. For orderliness of presentation, style of writing, figures, editorial details, and printing, etc., the book meets high standards of workmanship.

Needless to say, then, the reviewer heartily recommends this book for its intended purpose.

J. W. Williams
University of Wisconsin
Madison

Molecular Structure: The Physical Approach

J. C. D. Brand and *J. C. Speakman*, both of the University of Glasgow. St. Martin's Press, Inc., New York, 1960. (Edward Arnold (publishers) Ltd., London, 1960.) viii + 300 pp. Figs. and tables. 16 × 23.5 cm. $8.

Brand and Speakman's volume, judging from the title, should be a treatment of much the same material as Wheatley's "The Determination of Molecular Structure" (J. Chem. Educ., **36**, 636 (1959).) Both books are addressed to the nonspecialist. However, there the similarity ends, and the two books are more complementary than conflicting. Whereas Wheatley is greatly concerned with the experimental techniques, their pitfalls, difficulties, advantages, and particular range of application, Brand and Speakman devote a major portion of their space to to theoretical background and development of the methods and much less experimental detail and interpretation of results.

The book is a tremendously ambitious undertaking. It attempts to deal, not only with the methods used to determine structure in its geometrical sense, and to develop the theory of these methods, but includes the problems involving atomic motion; however, "matters connected explicitly with the properties of electrons in molecules have been excluded."

Following a general introduction, the authors follow a modern trend by giving a chapter on symmetry, and then introduce elementary wave mechanics. They then discuss, in detail, the rotation of molecules, nuclear resonance spectra, vibrations of molecules, and anisotropic polarizability and the Raman Effect. The diffraction methods, in two chapters on crystal structure analysis and electron diffraction, are given a much lighter treatment, because, the authors say in a somewhat philosophical chapter of appraisement and conclusion, "the spectroscopic methods look towards the wave function, (and therefore) constitute the most fundamental experimental approach to molecular structure."

The level at which this book is written varies. Some sections are completely mathematical, often beyond the level of comprehension of the typical American student, even at the first and second year graduate level, and certainly beyond the depth that the practicing experimental chemist in this country will generally pursue. Other sections, apparently where the mathematics gets a little tougher than the authors wish to cover, the text becomes completely qualitative and descriptive. An example is the NMR discussion, in which the basis of NMR spectra is treated in considerable mathematical detail, but such topics as spin coupling are simplified to the limit. This inhomogeneity is likely to discourage the reader interested only in a qualitative picture, and will leave the one interested in a thorough treatment dissatisfied after his appetite has been whetted. Unfortunately, some of the beautifully presented elegant mathematics introduced is largely lost because too little use of it is made in later development. A further discouragement to the uninitiated lies in the fact that the mathematics is often derived in the abstract, and only after the non-mathematical reader has given up, is the connection made to processes involving physical reality. Thus, for instance, a wave equation is solved in detail, as an introductory exercise in quantum mechanics and operator algebra; only in a later section does the reader realize that the exercise he performed was the solution of the wave equation for the harmonic oscillator, and thus has any physical interest. The mathematics is often too elegant; for the extremely limited use made of operators, a lengthy introduction into their meaning and algebra seems wasted. Similarly, the formalism of group theory, is so little used that its introduction does not seem essential.

In spite of these shortcomings, the book has much to offer. Particularly the student well-founded in mathematics and physics will find it stimulating and will be able to gain a basic insight into many areas with which he might not be familiar.

Technically, the book is well done and attractive. No misprints were noted. The lack of references to specific papers and investigations seems somewhat disturbing, particularly where data are quoted.

H. H. Jaffe
University of Cincinnati
Cincinnati, Ohio

Principles of Chemical Thermodynamics

Charles E. Reid, University of Florida, Gainesville. Reinhold Publishing Corp., New York, 1960. xii + 306 pp. Figs. and tables. 16 × 23.5 cm. College, $6, trade, $7.80.

In a noble attempt to resolve the confusion in thermodynamic nomenclature, the author unfortunately aggravates rather than alleviates the situation. In fairness, however, the reviewer must confess some resistance to change from nomenclature to which he is accustomed.

The commendable trend of chemical thermodynamic texts to divorce the heat engine from entropy is continued. The text is written in precise mathematical

(*Continued on page A40*)

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BY TERRELL L. HILL, *University of Oregon*

An introduction to equilibrium statistical mechanics, designed as a text for one or two-semester courses in chemistry departments or a one-semester course in physics departments, on the graduate level. The book provides a quite extensive coverage of topics of current interest. In fact, the more traditional material is treated in a rather condensed manner to allow ample room for a survey of the important developments of the 1940's and 1950's.

The first two chapters of the book develop the principles of statistical mechanics, based on elementary quantum-mechanical ideas. These principles are then applied in the next eleven chapters to systems of independent molecules or of other independent subsystems. The succeeding eight chapters treat the more complicated but interesting problems which arise when molecules can no longer be treated as independent of each other.

The concluding chapter, which requires somewhat more knowledge of quantum mechanics, deals with problems for which the classical (high temperature) limit of quantum statistics is *not* valid.

The text is quite flexible in usage, and broad in coverage. Numerous problems are included, ranging from simple numerical exercises to small-scale "research" problems. Those who are familiar with Professor Hill's previous book, *Statistical Mechanics* (which forms an introduction to the present text) will recognize that his new book is written in the same clear and thorough manner.

508 pp, 97 illus, 1960—$9.75

CHEMICAL INSTRUMENTATION:

A Systematic Approach to Instrumental Analysis

BY HOWARD A. STROBEL, *Duke University*

As the title indicates, the emphasis of this book is on the "science" of chemical instrumentation. Thus the student of instrumental analysis will gain from the text an understanding of the methods of identification, quantitative analysis, and measurement, which are operations common to all chemical research. He will also recognize future developments as but extensions of the basic techniques he has learned.

The most distinctive feature of the text is its attempt to convey a basic appreciation for the design and operation of instruments, as a part of the larger scheme of making physical measurements. To facilitate this appreciation, the book presents background chapters on the science of instrumentation, error analysis, interaction of electromagnetic radiation and matter, physical optics, electrical and electrochemical theory, and electronics.

Basic techniques are treated fully, and a good balance is maintained between physical theory and design on the one hand, and chemical theory and procedure on the other. Above all, the text offers a systematic approach to the basic principles common to all methods and types of instruments, rather than a mere catalog of equipment which is rapidly outdated. *653 pp, 373 illus, 1960—$9.75*

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language and may appear to some to be lacking a measure of "physical feeling" for thermodynamic concepts and functions. On the plus side, the chapters are short and easily read once familiarity with nomenclature is established. The number and quality of problems are adequate. The text is not intended to be as comprehensive in scope and application as Glasstone or Klotz. Accordingly there are less concrete examples and the problems are less numerous and practical than in either of these texts.

An introductory chapter to statistical thermodynamics is included for the benefit of students in their first and terminal graduate course of thermodynamics. This may be desirable but the chapter is decidedly lacking in fundamental quantum mechanical concepts which are covered superficially, if at all, in an elementary physical chemistry course, which, as the author states in the preface, is the only preparation necessary in chemistry. An introduction to statistical thermodynamics under such conditions is of questionable worth.

The last chapter deals with more sophisticated approaches to the evolution of interrelations between thermodynamic derivatives and includes the use of Jacobians, transformations of Koenig and Prins, among others. This chapter although intriguing to the mathematically inclined is of doubtful pedagogical or other value.

WILLIAM J. JAMES
University of Missouri
School of Mines and Metallurgy
Rolal

Henry Cavendish: His Life and Scientific Work

A. J. Berry, Fellow Emeritus of Downing College, Cambridge University. Hutchinson & Co., Ltd., London, 1960. 208 pp. Figs. 15 × 23.5 cm. 35/-.

The most recent extended treatment of Cavendish before this one, namely "Scientific Papers," edited by Larmor and Thorpe, appeared in 1921. This two-volume set was intended for specialists; hence the present text will be welcomed by the general reader. The author is completely at home in his subject and sympathetic in his approach; he has turned out a good book.

Henry Cavendish (1731–1810) like most of the natural philosophers of his era was both a chemist and physicist. He was a competent mathematician as well as a skilled manipulator, and was skilful in devising apparatus. Possessed of ample funds, he never held a paid position, and like his father was a true amateur. He was shy and reticent, and his biography makes rather dull reading if the incidents illustrating his eccentricities are omitted. To him, the outside world merely afforded opportunities for making measurements of volumes, weights, etc., activities which he accomplished in exemplary fashion. "When Cavendish's researches are viewed as a whole, certain features are character-

(*Continued on page A42*)

New Books Coming From McGraw-Hill . . . . .

THE DETERMINATION OF STABILITY CONSTANTS and Other Equilibrium Constants in Solution

By F. J. C. Rossotti and Hazel S. Rossotti, University of Edinburgh. McGraw-Hill Series in Advanced Chemistry. Ready in March, 1961.

A comprehensive guide to the study of complex formation in solution. The material is restricted to discussion of the experimental and computational methods used to study equilibria in solution. Emphasis is therefore placed on methods to determine equilibrium constants in systems where several species coexist. Concern throughout is focused on the intelligent design of experiments, careful measurements, and rigorous mathematical analysis.

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By Donald H. Menzel and Mrs. Lyle Boyd of the Harvard College Observatory, and Howard M. Jones, Harvard College. In Press.

This text stresses the problem of communication as it particularly relates to scientific writing. The chapters discuss the logical arrangement of data, the preparation of the physical manuscript, the intimate relation of grammar to clear expression, how simplicity of style produces clarity, and the futility of jargon.

HANDBOOK OF CHEMISTRY, Tenth Edition

By Norbert A. Lange, Professional Engineer. Ready in January, 1961.

A new revision of this long-regarded classic reference work. Formula weights of inorganic compounds, gravimetric and boiling points, solubilities, densities, and other material has been brought up-to-date in this latest edition.

CHEMISTRY, Second Edition

By M. J. Sienko and R. A. Plane, Cornell University. Ready in February, 1961.

A careful revision and improvement of this excellent textbook in college chemistry. Neither the character or the scope of the book has been changed, but the authors, with a multitude of reviewers, have reexamined and strengthened the first edition. The changes result in increased depth and lucidity rather than increased size. The aim of the book, as before, is to present an introductory course which is quantitative, up-to-date, and of sufficient rigor to prepare the student for further work in the field.

THERMODYNAMICS, New Second Edition

By G. N. Lewis and M. Randall (Revised by Kenneth S. Pitzer and Leo Brewer, both of the University of California, Berkeley). McGraw-Hill Series in Advanced Chemistry. Ready in February, 1961.

A revision by two top men in their field of a 1923 classic. The informal and much-admired style of the first edition has been retained and will make the book very appealing to all its readers. Because the last edition of the book was prepared 37 years ago, there is much new material included in the new edition, particularly in the middle and late chapters. These chapters have now been brought up to the present frontiers of thermodynamics. Illustrative materials have been brougnt up-to-date. As before, illustrative problems are worked out in considerable detail.

POLYMERIC MATERIALS

By Charles C. Winding, Cornell University, and Gordon D. Hiatt, Eastman Kodak Company. Ready in March, 1961.

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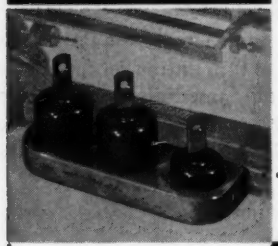

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istically predominant, notably a wide range of interests, a passion for accuracy, and a remarkable gift of making suitable choice of subjects worth investigating . . . ." "In most of his work his trend of thought seems to have been straight towards the course of the subsequent progress of science" (Sir Edward Thorpe).

After a chapter dealing with the ancestry and personal characteristics of Cavendish, the author sets the scene for Cavendish's researches by a masterly exposition of "physical and chemical science in the eighteenth century." Then follows a chapter on the chemical researches, which dealt mostly with "inflammable air," "fixed air," and the "air produced from vegetable and animal substances by distillation." His work is recounted in fair detail and his findings are put into their proper relationship with subsequent findings. Much of the material has been drawn from Cavendish's unpublished papers, of which there is a considerable amount. His eudiometric work is treated in sufficient detail, including his unwitting isolation of the rare gases of the atmosphere. The author, after due consideration, dubs him the founder of water analysis. The famed 'water controversy' is fairly presented in the chapter The Discovery of the Composition of Water. "The claims of Cavendish for priority over those of Lavoisier for having synthesized water from its elements were thus clearly demonstrated." Cavendish, of course, maintained that there was no reason for relinquishing the phlogistic hypothesis, nor for adopting the new *Nomenclature chimique*, remarking that "It has only served the more to convince me of the impropriety of systematic names in chemistry and the great mischief that will follow from his (Lavoisier's) scheme if it should come into use."

Four chapters of the volume under review are devoted to the purely physical investigations, namely two chapters on the electrical researches, one on the researches on heat, and finally a chapter devoted to the meteorological subjects. This latter chapter is chiefly taken up with the famous "Cavendish experiment," in which he made an outstanding determination of the density of the earth. Since these chapters contain principally discussions of topics primarily related to physics, they will not be analyzed here but they can be highly recommended to students of the history of physics and physical chemistry.

The concluding chapter deals with Cavendish and Modern Science. Here Cavendish and his work are considered from the standpoint of the subsequent developments. He emerges with flying colors. A reading of this chapter will all the more impress the reader of this fine book with the aptness of the opening sentence in which reference is made to "Henry Cavendish, one of the greatest scientific discoverers of all time."

RALPH E. OESPER
University of Cincinnati
Cincinnati, Ohio

(Continued on page A44)

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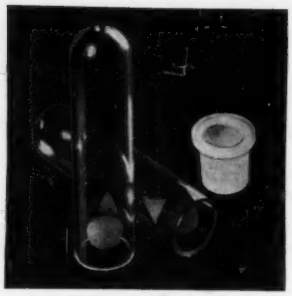

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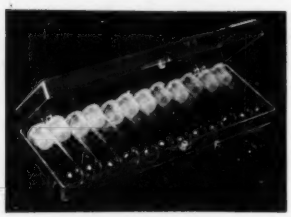

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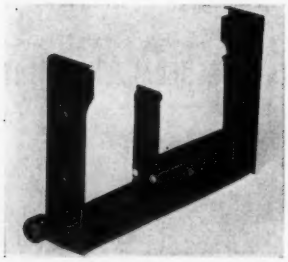

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BOOK REVIEWS

Quantitative Inorganic Analysis

R. Belcher, University of Birmingham, England, and *A. J. Nutten*, Government Laboratory, Hong Kong. 2nd ed. (Butterworths Scientific Publications) Butterworths & Co. (Canada) Ltd., Toronto, 1960. x + 390 pp. Figs. and tables. 16 × 25 cm. $7.

As stated on the dust jacket, this book is "A Laboratory Manual for Students and Practising Chemists." As such it has much more emphasis on the anlytical procedures and less on chemical equilibrium theory than most of the current books on quantitative analysis used in colleges and universities in this country.

This second edition is in general like the first with some modifications in the procedures deemed desirable in light of experience or where new methods or materials have become available.

The first section of the book deals with the usual introduction to analytical work: cleaning of equipment, methods of filtration, procedures for weighing, etc. It is interesting to note that these authors believe the swinging pointer balance to be obsolete so that analysts should be trained on aperiodic or single pan balances.

Each group of analytical procedures is preceded by a discussion of the general principles involved in this type of analysis. A particular analytical procedure is introduced by a general discussion of the method followed by a section on the interferences to be expected. The detailed procedure for the analysis is then given, followed by the method for calculation of the results. In several instances, additional methods for the same determination are given, sometimes in detail and sometimes in general terms. Each section is concluded with a generous list of references.

There is no wasted space in this book. Although it contains only some 370 pages there are included the following numbers of analytical procedures: gravimetric, 24; titrimetric, 70; colorimetric, 7; plus some potentiometric titrations, electrolytic analyses and industrial analyses such as steel, brass, and limestone.

In addition to the numerous analytical procedures there are short sections on theory of precipitation, acid-base relationships and theory of indicators, colorimetry, adsorption indicators, and balancing oxidation-reduction equations. These sections are brief and it is apparently the authors intention that the reader should consult other books for further development of the theory.

As a laboratory manual or a reference book on most ordinary analyses of inorganic chemistry this book seems very adequate. As a textbook for the teacher who wishes to emphasize chemical equilibria in quantiative analysis this book would have to be supplemented by other sources.

PAUL K. GLASOE
Wittenberg University
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(Continued on page A46)

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A Statistical Manual for Chemists

Edward L. Bauer, Winthrop Laboratories, Rensselaer, New York. Academic Press, Inc., New York, 1960. x + 156 pp. Figs. and tables. 14 × 21 cm. $4.75.

It is being increasingly recognized that modern statistics provides the chemist with a sharp tool of wide applicability. Several books have appeared in which statistics is presented via chemical examples. "A Statistical Manual for Chemists" by E. L. Bauer is the latest addition to this group.

The author presents a sub-elementary and very limited view of statistical methods. The comparison of two and of more than two averages, some of the elements of experimental design, regression, sampling, and the use of quality control techniques in the analytical laboratory are mentioned. The book concludes with a collection of nine tables designed to provide the necessary critical values for the techniques propounded.

Virtually all of the procedures described employ the range as an estimator of the population standard deviation in place of the conventional standard deviation estimate. Unfortunately, however, the reader is not given any basis for evaluating the author's statement (p. 11) that "... the range is accurate enough for practical purposes." (Actually, *efficiency* rather than accuracy is in question.) Although range techniques have their place, the same information concerning variability is obtained from nine observations with the range as from eight observations using the standard deviation estimate. By increasing the statistical work in that eight numbers must be squared, one can cut back the experimental work by a little more than 10 per cent. The choice should be the experimenter's.

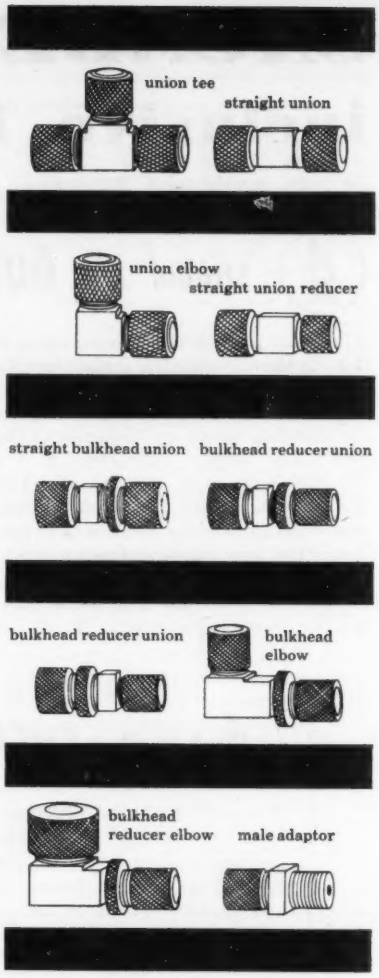
Nevertheless, even granting that the author has made an appropriate decision for the experimenter in regard to the use of the range, this book must be severely criticized for the many misleading phrases and numerous incorrect statements it contains.

Hypotheses, tests of significance, confidence intervals, multiple comparisons, and regression analysis are taken up by the author. Within every one of these topics there are glaring mistakes of either explanation or interpretation. Inconsistent terminology adds to the confusion. Experimental design is discussed but the term interaction is not fully explained and the subject of randomization (essential in statistics) is by-passed completely.

The distinction, which is of fundamental importance, between a statistical parameter and a statistic (a value which estimates a parameter) is not made clear. The reader is not shown the central role played by the null hypothesis in significance testing; nor is he given any inkling that hypothesis testing is not limited to zero-difference null hypotheses. On page 17 confidence intervals (incorrectly described) are wrongly interpreted as tolerance intervals.

The uncertainty calculated for the

(*Continued on page A48*)



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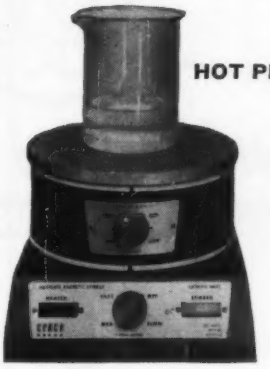

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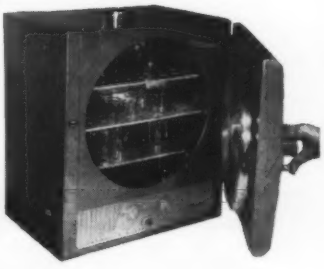

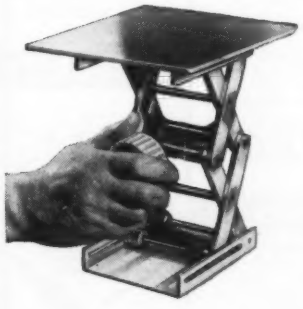

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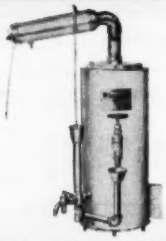

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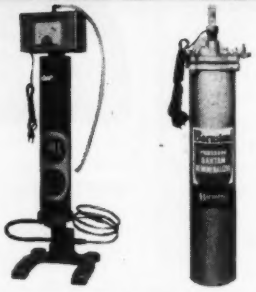

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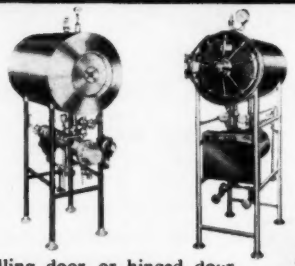

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predicted value obtained from the regression analysis on page 103 is too small by a factor of 30. The procedure which the author should have followed is clearly outlined in the second reference given on that same page. On page 134 the normal distribution is described as having 23 per cent of its area and 5 per cent of its area above points one and two standard deviations up from the mean, respectively. Both of these values are quite wrong, but the reader will have to check this fact elsewhere because this book does not have a table of the normal distribution.

The preceding criticisms are only a small sample of what is wrong with this book. Anyone attempting to learn the subject of statistics or any part of it with the aid of this manual will be getting off to a very bad start.

LLOYD S. NELSON
General Electric Lamp Division
Cleveland 12, Ohio

Optical Rotatory Dispersion: Applications to Organic Chemistry

Carl Djerassi, Stanford University, California, and Syntex (S. A.), Mexico City. McGraw-Hill Book Co., Inc., New York, 1960. xiii + 293 pp. Figs. and table. 15.5 × 23.5 cm. $7.50.

It has been a long time since P. A. Levene and Alexandre Rothen wrote their chapter on "Rotatory Dispersion" for the first edition of Gilman's "Organic Chemistry, an Advanced Treatise," to which most graduate students in chemistry have been exposed at least in part. Newer applications and the recent accumulation of reported research have made it desirable to have an authoritative modern treatment. This is edited and largely written by Carl Djerassi of Stanford University under the title of "Optical Rotatory Dispersion." Other writers who have contributed substantially are Albert Moscowitz, the late William Moffitt, Elkan R. Blout, and John A. Schellman.

The book opens with a preface telling of the necessity to undertake such a writing because of the gap since the publication of T. M. Lowry's "Optical Rotatory Power" in 1934. There follows seventeen chapters bearing the titles: Introduction; Nomenclature; Instrumentation; Steroids; Bicyclic Ketones; Triterpenoids; Monocyclic Aliphatic Carbonyl Compounds; α-Hydroxy Ketones; α-Halo ketones; Determination of Absolute Configuration; Detection and Implication of Ketal Formation; Theory and Analysis of Rotatory Dispersion Curves; Octant Rule; Thiones, Nitroalkanes, and Other Chromophores; Alcohols; α-Hydroxy Acids, and α-Amino Acids; Plain Dispersion Curves; Polypeptides and Proteins. There are two appendixes: A. Bibliography, with a concise review of earlier literature, a concise review of later literature and an extensive list of publications of Carl Djerassi; B. Nomenclature and Stereochemical Conventions, with reference to Steroids and Triterpenoids. Author and compound indexes are supplied. Tables, graphs, formulas, and diagrams are used effectively and clearly throughout the chapters.

(*Continued on page A50*)

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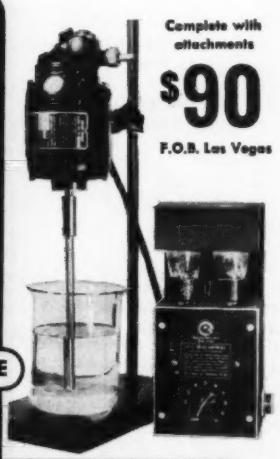

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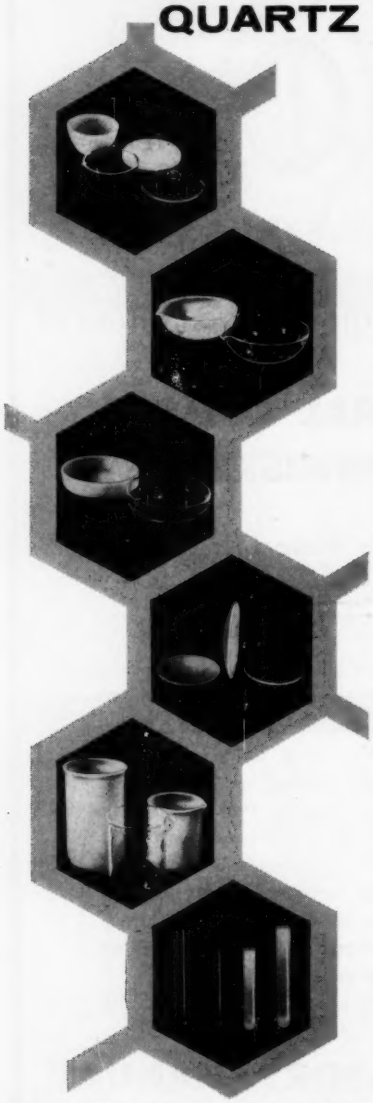

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This book is obviously intended for research workers in the field and as an introduction to the neophyte who wishes to get started quickly. It will find wide usage for most persons interested in stereochemistry or molecular biology and will provide a reference or even a text for special types of graduate courses and seminars, and perhaps some of the more advanced undergraduate courses. Conformation, absolute configuration, and many more complex related problems can be solved through this useful technique. Not only is the theory presented succinctly, but practical aspects like those related to the fine points of very high precision instrumentation and their development are enlarged upon.

To say that this text will be exceedingly useful is, of course, trite. It will entice many people into this field of research and will cause the development of finer instruments, modifications of which will no doubt become commercially available even with automatic recording. Solutions to problems like the nature of muscle contraction and expansion and the kinds of folding and coiling of certain enzymes will be partially elucidated through usage of these instruments. As a result, it will not be too long before Carl Djerassi will find it necessary to make an early revision to keep pace with the growing information.

JOHN LEO ABERNETHY
University of Redlands
Redlands, California

Engineering Thermodynamics: An Introductory Textbook

James B. Jones and *George A. Hawkins*, both of Purdue University, Lafayette, Indiana. John Wiley & Sons, Inc., New York, 1960. xviii + 724 pp. Figs. and tables. 15.5 × 23.5 cm. $8.50.

The authors state that this book is intended for use in undergraduate engineering courses in thermodynamics. It is this reviewer's opinion that there would be a great amount of overlapping if this text were used for chemical engineering students. Many of the chapters are covered, often in greater detail, in the energy and material balance courses in chemical engineering and also in physical chemistry courses.

The book is written in a clear manner with considerable detail so that most of the content could be understood by the student at first reading. Over 700 problems are presented for practice purposes. The book contains many illustrated problems and solutions. It is interesting that the authors, although mechanical engineers, make use of the mole to a great extent.

It is doubtful whether this book will be adopted by chemical engineering departments if the staff members have a choice.

JOHN J. MCKETTA
The University of Texas
Austin

(Continued on page A52)

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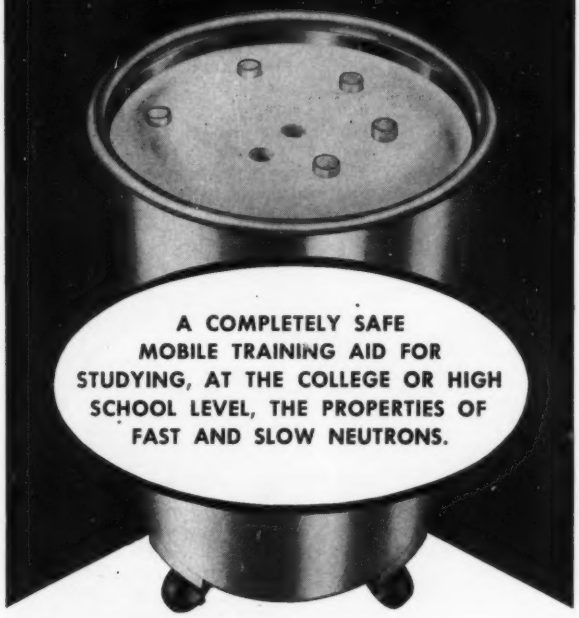

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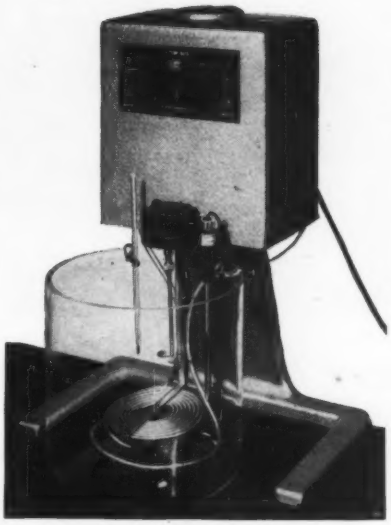

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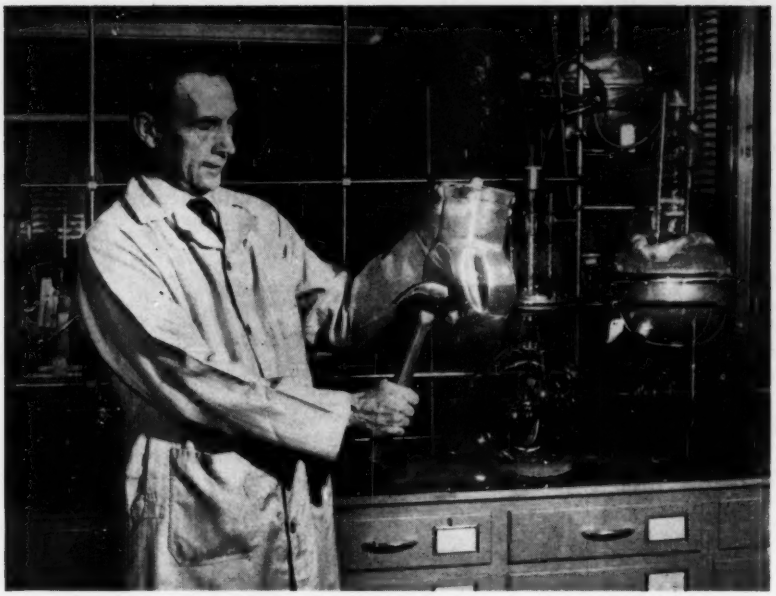

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Chemical Analysis. Volume 12: Systematic Analysis of Surface-Active Agents

Milton J. Rosen, Brooklyn College, Brooklyn, New York, and *Henry A. Goldsmith*, Turco Products, Inc., Los Angeles, California. Interscience Publishers, Inc., New York, 1960. xvii + 422 pp. Figs. and tables. 16 × 23.5 cm. $13.50.

Surface active agents are generally manufactured as complex mixtures of closely related products; they are then often compounded with other surfactants and with various additives, and this material may finally be used as a minor constituent of a final product such as a cutting oil or a cosmetic. The book of Rosen and Goldsmith deals in a systematic manner with the problem of separating the surfactants from other materials and of analyzing them qualitatively and quantitatively. Most of the book is devoted to newly developed analytical schemes which blend a selection of old methods with original contributions by the authors and are based on a new classification of surfactants for analytical purposes. The book is addressed to the mature chemist and is concerned primarily with the "how" and "what does it mean" of a procedure rather than the details of the "why" of it.

For those concerned with the analysis of surfactants this book will be invaluable both as a source of tested procedures and as a guide to the widely scattered literature of this field.

KAROL J. MYSELS
University of Southern California
Los Angeles

The Principles of Electrophoresis

Rene Audubert, formerly Professor at the Sorbonne (deceased) and *Serge de Mende*, National Centre for Scientific Research, Paris. Translated by *A. J. Pomerans*. The Macmillan Co., New York, 1960. viii + 142 pp. Figs. and tables. 15 × 23.5 cm. $7.

Electrophoresis in Physiology

Lena A. Lewis, Cleveland Clinic, Cleveland, Ohio, with a special chapter by *M. D. Poulik*, Child Research Center of Michigan, Detroit. 2nd ed. Publication No. 385, American Lecture Series. Charles C Thomas, Springfield, Illinois, 1960. v + 120 pp. Figs. and tables. 16 × 23.5 cm. $5.50.

These two books duplicate each other in the description of apparatus and methods, but for the most part are complementary. Audubert and de Mende devote one chapter of nine to specific applications of electrophoresis, while Lewis discusses applications in physiology through nearly two-thirds of her book.

The first four chapters of "The Principles of Electrophoresis" are introductory, beginning with elementary theory of electrolyte and colloidal solutions. Electrokinetic potential, electro-osmosis, and the determination of mobilities of simple

(*Continued on page A54*)

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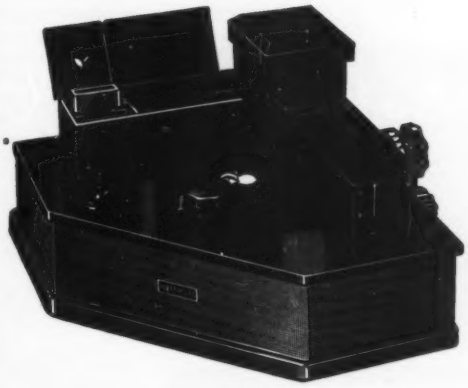

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ions are included. One chapter each on the moving-boundary method and electrophoresis in a supporting medium are the largest and most important.

The commercial apparatus available for both types of electrophoresis (European models) and the optical systems used to detect the boundaries in solution electrophoresis are covered in some detail. Particular attention is given to the effect of buffer flow in paper electrophoresis and how its influence can be minimized or corrected. Another chapter covers the practical use of paper electrophoresis, including such topics as detection methods, quantitative measurements, and mobility equilibria. A brief discussion of preparative electrophoresis in gels, columns, and on a hanging curtain of paper and a chapter on applications end the book.

The treatment given is fairly complete, especially for such a small book, and offers many practical suggestions which should be useful to a beginner in the field. It does not give a long series of specific uses, but does include enough examples to illustrate the points discussed.

In contrast to this, Lewis has written a more limited book, with only 30 pages of general discussion preceding the physiological applications. Nearly half of the book is devoted to step-by-step instructions for electrophoresis of different types, a list of equipment manufacturers, and the bibliography. A short chapter on immuno-electrophoresis illustrates the possibilities of this method and the complexity of proteins, even when apparently homogeneous according to other methods.

For a general introduction to electrophoresis, in both theory and practice, Audubert and de Mende is very good. Lewis' book will be much less useful to chemists.

DONALD A. TARR
The College of Wooster
Wooster, Ohio

Advances in Protein Chemistry. Volume 14

Edited by *C. B. Anfinsen, Jr.*, National Heart Institute, Bethesda, Maryland, *M. L. Anson*, London, England, *Kenneth Bailey*, University of Cambridge, England, and *John T. Edsall*, Harvard University, Cambridge, Massachusetts. Academic Press, Inc., 1959. xxiii + 520 pp. Figs. and tables. 16 × 23.5 cm. $14.

The current volume of this series differs from the previous ones in that it contains a concise biography of Kaj U. Linderstrøm-Lang, who died in Copenhagen in 1959. Written by Dr. John T. Edsall, the obituary is not only a tribute to one of the outstanding pioneers in biochemistry, but also an excellent historical survey of much of the fundamental theories and substantiating experimental work pertaining to the physico-chemical properties and molecular structures of proteins.

The remainder of the book is similar to previous volumes, consisting of thorough reviews, with extensive bibliographies, of the accomplishments of the

(*Continued on page A56*)

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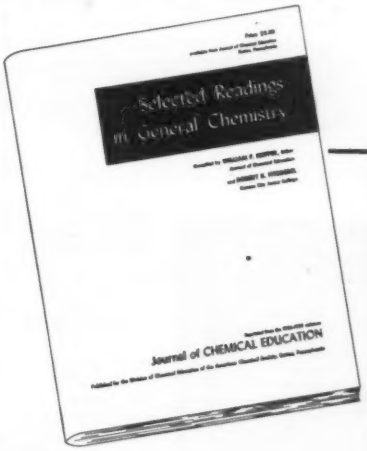

"Selected Readings in General Chemistry," is a 128-page collection of over 40 papers which have appeared in dozens of separate issues of the *Journal of Chemical Education* during the last three years. On the list of authors, such names as Calvin, Libby, Nyholm, Pauling, and Williams are recognized by chemists everywhere. Topics range from spontaneous generation of life to solid state models, and from antiknock quality in gasoline out into space with the IGY and amateur rocketry.

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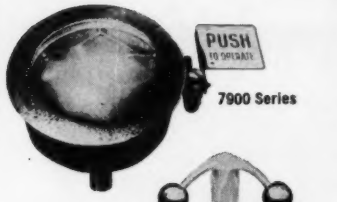

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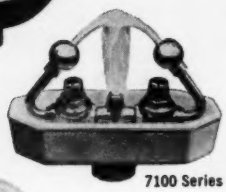

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last 20 years in several aspects of protein chemistry. Recently developed techniques, theories, and interpretations are given, and enough experimental data are included to permit evaluation of the validity of the conclusions.

The first review, by W. Kauzmann, is a critical and thorough summary of the various factors involved in the interpretation of the processes of protein denaturation.

Various applications of the technique of zone electrophoresis in starch gels to the separation and identification of the proteins in blood serum are presented in the second article by O. Smithies.

The third review, by Martha Vaughan and Daniel Steinberg, is entitled "The Specificity of Protein Biosynthesis." The section on genetic determination of amino acid sequences is especially thorough including a table of proteins and polypeptides in which certain amino acid sequences are known to be genetically determined and a critical discussion of the one-gene-one-enzyme hypothesis. Much of the work involving the synthesis, by microorganisms, of enzymes containing analogues is described. The authors conclude that "all the evidence obtained to date . . . points to the specificity of protein biosynthesis."

In the fourth article, by H. Fraenkel-Conrat and L. K. Ramachandran, many of the concepts and techniques discussed in the third review are applied to the elucidation of the structure of tobacco mosaic virus. A noteworthy feature of the review is a thorough discussion of the functional relationships between the protein and nucleic acid components, especially with respect to significant differences between the properties of the intact virus and the viral RNA.

The brevity of the fifth review, by R. A. Kekwick, indicates the paucity of knowledge pertaining to the serum proteins of the fetus and young of mammals. Most of the data summarize the available information with respect to the percentages of total protein and of albumin, the several globulins and fibrinogen in the blood of fetuses and young of several species, chiefly humans, bovines, sheep, rabbits, and rats.

The sixth review, by R. Cecil and J. R. McPhee, should be of interest to organic chemists as well as to biochemists, since most of it is concerned with the comparative reactions of and analytical methods for determining thiols, disulfides, and thioethers. In the last third of the article the knowledge obtained by applying these methods to 13 different proteins is presented.

The last article in the volume, by Michael Sela and Ephraim Katchalski, summarizes the biological properties of poly-*alpha*-amino acids. The emphasis in this review is on the physical, chemical, and biological properties of various polymers of *alpha*-amino acids, rather than on methods for preparing them. The usefulness of these polymers in studying the actions of known proteolytic enzymes as well as in discovering new ones is well documented.

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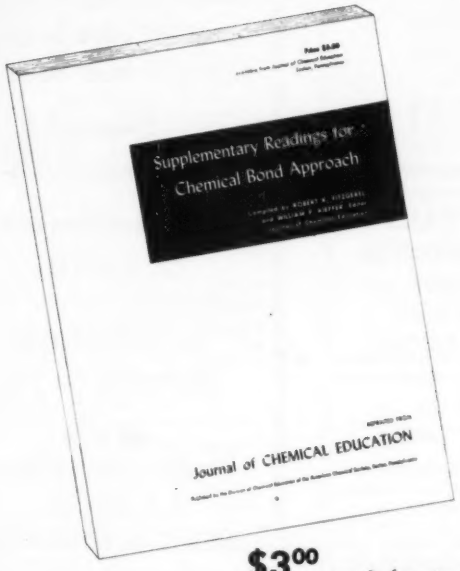

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Many modern interpretations of chemical bonding are developed further than usually found in textbooks. The variety of approaches is itself stimulating to the inquiring reader. The obvious feature common to the whole collection is that these have been written by authors whose successful experience with students has shaped their presentation.

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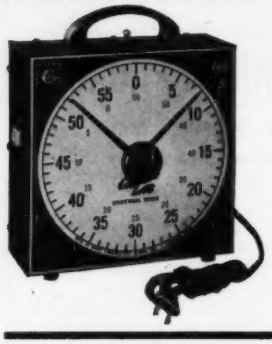

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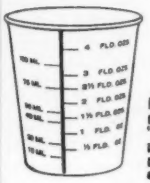

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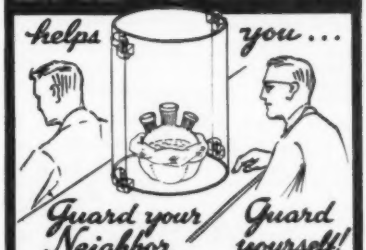

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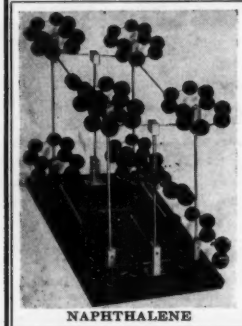

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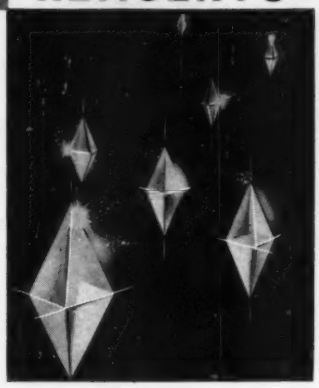

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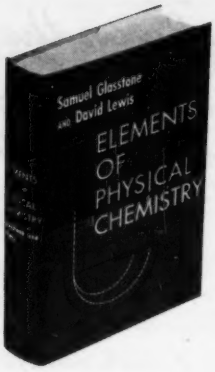

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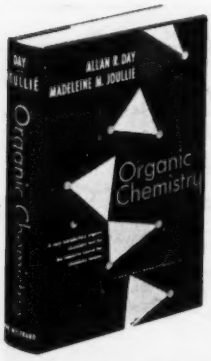

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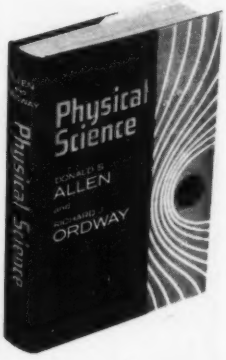

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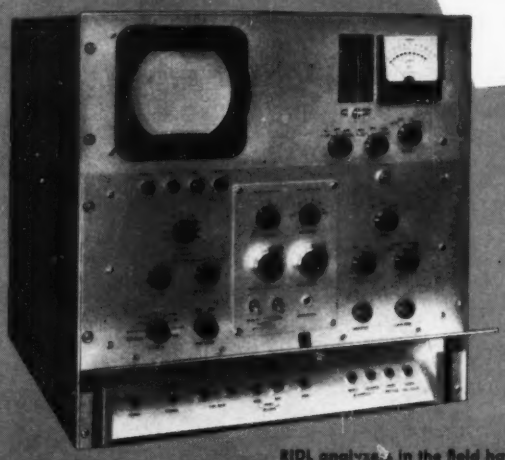

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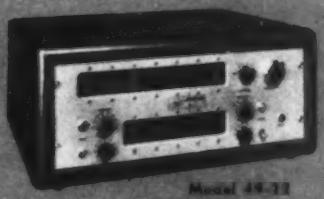

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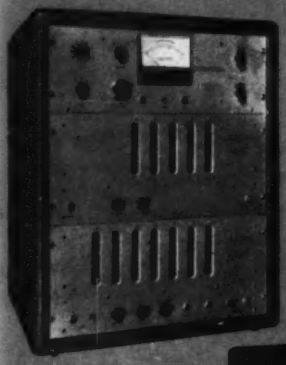

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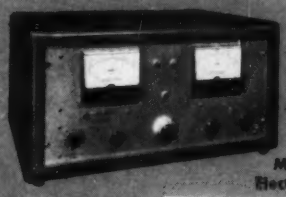

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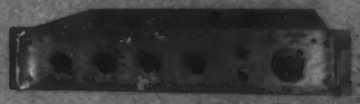

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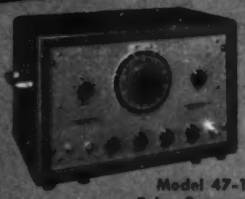

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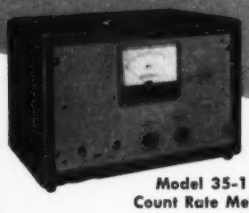

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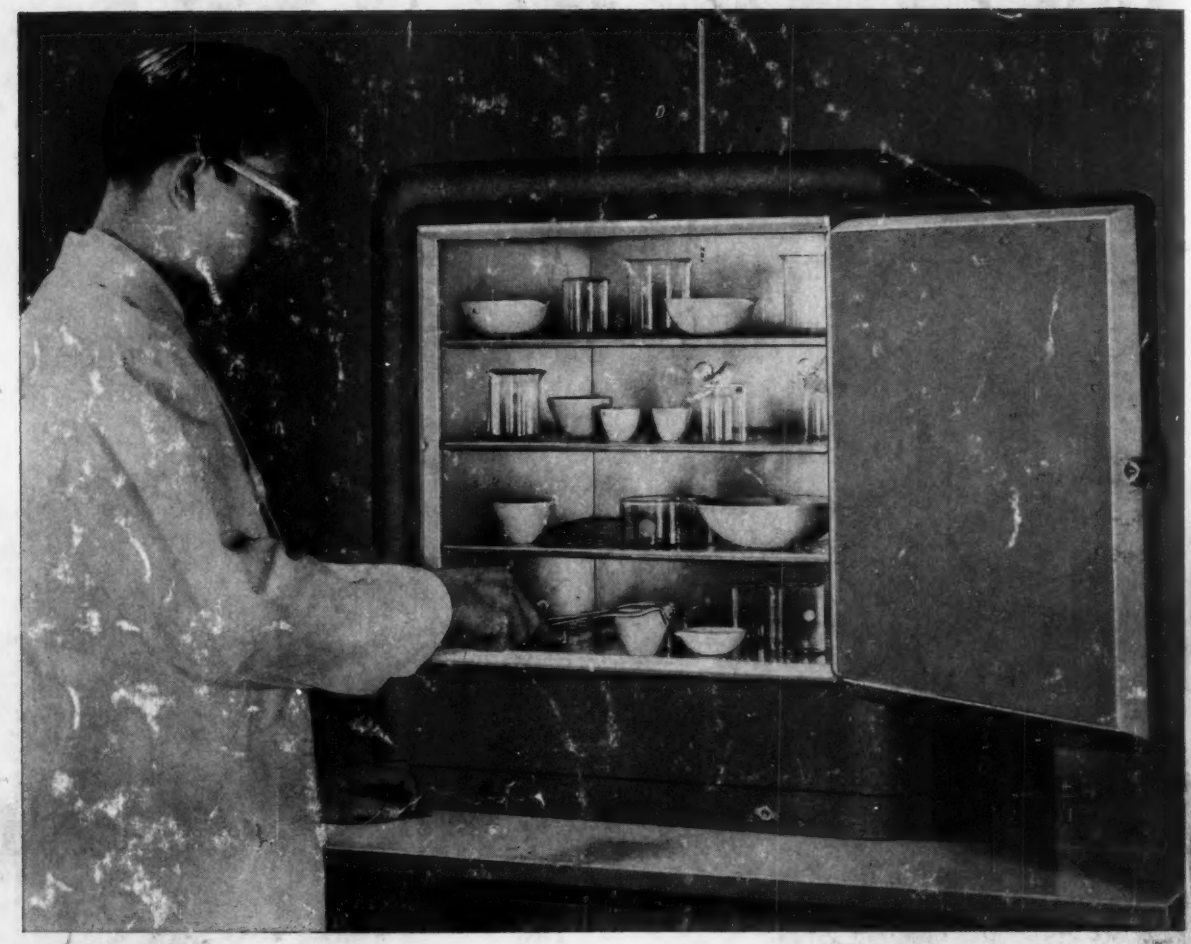

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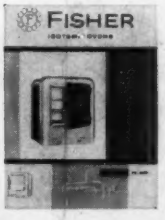

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